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## (54) **NONAQUEOUS ELECTROLYTE AND NONAQUEOUS ELECTRLYTE SECONDARY CELL**

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a nonaqueous electrolyte which can restrain expansion of an envelope caused by generation of gas when it is preserved in high temperature and self-discharge at high temperature, and capable of improving charge-discharge cycle property.

**SOLUTION:** Nonaqueous solvent included in nonaqueous electrolyte contains the fourth component composed of one or more kinds of solvent selected from a group of ethylene carbonate(EC), propylene carbonate(PC),  $\gamma$ -butyrolactone(BL), vinylene carbonate, vinylethylene carbonate, ethylene sulfate, phenylethylene carbonate, 12-crown-4, and tetraethylene glycol dimethyl ether, and when the volume content ratio (vol.%) of EC, PC, BL, and the fourth component are made x, y, z, and p respectively, the relations  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0 < p \leq 5$  are fulfilled.

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## CLAIMS

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[Claim(s)]

[Claim 1] In the nonaqueous electrolyte possessing a non-aqueous solvent and the lithium salt dissolved in said non-aqueous solvent said non-aqueous solvent Ethylene carbonate, propylene carbonate, and gamma-butyrolactone, Ethylene carbonate [ as opposed to said whole non-aqueous solvent including the 4th component except said ], The rate of propylene carbonate, gamma-butyrolactone, and said 4th component, respectively x (volume %), It is nonaqueous electrolyte characterized by said x, said y, said z, and said p filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0 < p \leq 5$ , respectively when referred to as y (volume %), z (volume %), and p (volume %).

[Claim 2] In the nonaqueous electrolyte possessing a non-aqueous solvent and the lithium salt dissolved in said non-aqueous solvent said non-aqueous solvent Ethylene carbonate, propylene carbonate, and gamma-butyrolactone, Vinylene carbonate, vinyl ethylene carbonate, an ethylene ape fight, The 4th component which consists of one or more kinds of solvents chosen from the group which consists of phenylethylene carbonate, 12-crown -4, and tetraethylene glycol wood ether is included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone and said 4th component, respectively x (volume %), It is nonaqueous electrolyte characterized by said x, said y, said z, and said p filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0 < p \leq 5$ , respectively when referred to as y (volume %), z (volume %), and p (volume %).

[Claim 3] In the nonaqueous electrolyte possessing a non-aqueous solvent and the lithium salt dissolved in said non-aqueous solvent said non-aqueous solvent Ethylene carbonate, propylene carbonate, and gamma-butyrolactone, Ethylene carbonate [ as opposed to said whole non-aqueous solvent including vinylene carbonate and the 5th component except said ], The rate of propylene carbonate, gamma-butyrolactone, vinylene carbonate, and said 5th component, respectively x (volume %), It is nonaqueous electrolyte characterized by said x, said y, said z, said w, and said q filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,

$30 \leq z \leq 85$ ,  $0 < w \leq 5$ , and  $0 < q \leq 5$ , respectively when referred to as y (volume %), z (volume %), w (volume %), and q (volume %).

[Claim 4] In the nonaqueous electrolyte possessing a non-aqueous solvent and the lithium salt dissolved in said non-aqueous solvent said non-aqueous solvent Ethylene carbonate, propylene carbonate, and gamma-butyrolactone, Vinylene carbonate, vinyl ethylene carbonate, an ethylene ape fight, The 5th component which consists of one or more kinds of solvents chosen from the group which consists of phenylethylene carbonate, 12-crown -4, and tetraethylene glycol wood ether is included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone, vinylene carbonate, and said 5th component, respectively x (volume %), It is nonaqueous electrolyte characterized by said x, said y, said z, said w, and said q filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ ,  $0 < w \leq 5$ , and  $0 < q \leq 5$ , respectively when referred to as y (volume %), z (volume %), w (volume %), and q (volume %).

[Claim 5] A non-aqueous solvent and the lithium salt dissolved in said non-aqueous solvent are provided. Said non-aqueous solvent Ethylene carbonate, propylene carbonate, gamma-butyrolactone, and vinylene carbonate are included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone and vinylene carbonate, respectively x (volume %), It is nonaqueous electrolyte characterized by said x, said y, said z, and said w filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0.05 \leq w \leq 5$ , respectively when referred to as y (volume %), z (volume %), and w (volume %).

[Claim 6] In the nonaqueous electrolyte rechargeable battery possessing the nonaqueous electrolyte in which thickness contains the lithium salt which it is held at a sheathing material 0.3mm or less, the electrode group contained in said sheathing material, and said electrode group, and dissolves in a non-aqueous solvent and said non-aqueous solvent Said non-aqueous solvent Ethylene carbonate and propylene carbonate, Ethylene carbonate [ as opposed to said whole non-aqueous solvent including gamma-butyrolactone and the 4th component except said ], The rate of propylene carbonate, gamma-butyrolactone, and said 4th component, respectively x (volume %), It is the nonaqueous electrolyte rechargeable battery characterized by said x, said y, said z, and said p filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0 < p \leq 5$ , respectively when referred to as y (volume %), z (volume %), and p (volume %).

[Claim 7] In the nonaqueous electrolyte rechargeable battery possessing the nonaqueous electrolyte in which thickness contains the lithium salt which it is held at a sheathing material 0.3mm or less, the electrode group contained in said sheathing material, and said electrode group, and dissolves in a non-aqueous solvent and said non-aqueous solvent Said non-aqueous solvent Ethylene carbonate and propylene carbonate, Gamma-butyrolactone, and vinylene carbonate, vinyl ethylene carbonate, The 4th component which consists of one or more kinds of solvents chosen from the group which consists of an ethylene ape fight, phenylethylene carbonate, 12-crown -4, and tetraethylene glycol wood ether is included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone and said 4th component, respectively x (volume %), It is the nonaqueous electrolyte rechargeable battery characterized by said x, said y, said z, and said p filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0 < p \leq 5$ , respectively when referred to as y (volume %), z (volume %), and p (volume %).

[Claim 8] In the nonaqueous electrolyte rechargeable battery possessing the nonaqueous

electrolyte in which thickness contains the lithium salt which it is held at a sheathing material 0.3mm or less, the electrode group contained in said sheathing material, and said electrode group, and dissolves in a non-aqueous solvent and said non-aqueous solvent Said non-aqueous solvent Ethylene carbonate and propylene carbonate, Gamma-butyrolactone, vinylene carbonate, and the 5th component except said are included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone, vinylene carbonate, and said 5th component, respectively x (volume %), It is the nonaqueous electrolyte rechargeable battery characterized by said x, said y, said z, said w, and said q filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ ,  $0 < w \leq 5$ , and  $0 < q \leq 5$ , respectively when referred to as y (volume %), z (volume %), w (volume %), and q (volume %).

[Claim 9] In the nonaqueous electrolyte rechargeable battery possessing the nonaqueous electrolyte in which thickness contains the lithium salt which it is held at a sheathing material 0.3mm or less, the electrode group contained in said sheathing material, and said electrode group, and dissolves in a non-aqueous solvent and said non-aqueous solvent Said non-aqueous solvent Ethylene carbonate and propylene carbonate, Gamma-butyrolactone, vinylene carbonate, and vinyl ethylene carbonate, The 5th component which consists of one or more kinds of solvents chosen from the group which consists of an ethylene ape fight, phenylethylene carbonate, 12-crown -4, and tetraethylene glycol wood ether is included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone, vinylene carbonate, and said 5th component, respectively x (volume %), It is the nonaqueous electrolyte rechargeable battery characterized by said x, said y, said z, said w, and said q filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ ,  $0 < w \leq 5$ , and  $0 < q \leq 5$ , respectively when referred to as y (volume %), z (volume %), w (volume %), and q (volume %).

[Claim 10] Said nonaqueous electrolyte is a nonaqueous electrolyte rechargeable battery claim 6 characterized by liquefied or having a gel gestalt - given in 9 any 1 terms.

[Claim 11] The positive electrode and negative electrode with which thickness is contained in a sheathing material 0.3mm or less and said sheathing material, In the nonaqueous electrolyte rechargeable battery possessing the electrolyte layer containing the polymer which has the function for it to be arranged between said positive electrode in said sheathing material, and said negative electrode, and to make nonaqueous electrolyte and said nonaqueous electrolyte gel Said nonaqueous electrolyte contains the lithium salt dissolved in a non-aqueous solvent and said non-aqueous solvent. Said non-aqueous solvent Ethylene carbonate, propylene carbonate, and gamma-butyrolactone, Ethylene carbonate [ as opposed to said whole non-aqueous solvent including the 4th component except said ], The rate of propylene carbonate, gamma-butyrolactone, and said 4th component, respectively x (volume %), It is the nonaqueous electrolyte rechargeable battery characterized by said x, said y, said z, and said p filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0 < p \leq 5$ , respectively when referred to as y (volume %), z (volume %), and p (volume %).

[Claim 12] The positive electrode and negative electrode with which thickness is contained in a sheathing material 0.3mm or less and said sheathing material, In the nonaqueous electrolyte rechargeable battery possessing the electrolyte layer containing the polymer which has the function for it to be arranged between said positive electrode in said sheathing material, and said negative electrode, and to make nonaqueous

electrolyte and said nonaqueous electrolyte gel Said nonaqueous electrolyte contains the lithium salt dissolved in a non-aqueous solvent and said non-aqueous solvent. Said non-aqueous solvent Ethylene carbonate, propylene carbonate, and gamma-butyrolactone, Vinylene carbonate, vinyl ethylene carbonate, an ethylene ape fight, The 4th component which consists of one or more kinds of solvents chosen from the group which consists of phenylethylene carbonate, 12-crown -4, and tetraethylene glycol wood ether is included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone and said 4th component, respectively x (volume %), It is the nonaqueous electrolyte rechargeable battery characterized by said x, said y, said z, and said p filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0 < p \leq 5$ , respectively when referred to as y (volume %), z (volume %), and p (volume %).

[Claim 13] The positive electrode and negative electrode with which thickness is contained in a sheathing material 0.3mm or less and said sheathing material, In the nonaqueous electrolyte rechargeable battery possessing the electrolyte layer containing the polymer which has the function for it to be arranged between said positive electrode in said sheathing material, and said negative electrode, and to make nonaqueous electrolyte and said nonaqueous electrolyte gel Said nonaqueous electrolyte contains the lithium salt dissolved in a non-aqueous solvent and said non-aqueous solvent. Said non-aqueous solvent Ethylene carbonate, propylene carbonate, and gamma-butyrolactone, Ethylene carbonate [ as opposed to said whole non-aqueous solvent including vinylene carbonate and the 5th component except said ], The rate of propylene carbonate, gamma-butyrolactone, vinylene carbonate, and said 5th component, respectively x (volume %), It is the nonaqueous electrolyte rechargeable battery characterized by said x, said y, said z, said w, and said q filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ ,  $0 < w \leq 5$ , and  $0 < q \leq 5$ , respectively when referred to as y (volume %), z (volume %), w (volume %), and q (volume %).

[Claim 14] The positive electrode and negative electrode with which thickness is contained in a sheathing material 0.3mm or less and said sheathing material, In the nonaqueous electrolyte rechargeable battery possessing the electrolyte layer containing the polymer which has the function for it to be arranged between said positive electrode in said sheathing material, and said negative electrode, and to make nonaqueous electrolyte and said nonaqueous electrolyte gel Said nonaqueous electrolyte contains the lithium salt dissolved in a non-aqueous solvent and said non-aqueous solvent. Said non-aqueous solvent Ethylene carbonate, propylene carbonate, and gamma-butyrolactone, Vinylene carbonate, vinyl ethylene carbonate, an ethylene ape fight, The 5th component which consists of one or more kinds of solvents chosen from the group which consists of phenylethylene carbonate, 12-crown -4, and tetraethylene glycol wood ether is included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone, vinylene carbonate, and said 5th component, respectively x (volume %), It is the nonaqueous electrolyte rechargeable battery characterized by said x, said y, said z, said w, and said q filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ ,  $0 < w \leq 5$ , and  $0 < q \leq 5$ , respectively when referred to as y (volume %), z (volume %), w (volume %), and q (volume %).

[Claim 15] In the nonaqueous electrolyte rechargeable battery possessing the nonaqueous electrolyte in which thickness contains the lithium salt which it is held at a sheathing material 0.3mm or less, the electrode group contained in said sheathing material, and said

electrode group, and dissolves in a non-aqueous solvent and said non-aqueous solvent Said non-aqueous solvent Ethylene carbonate, propylene carbonate, Ethylene carbonate [ as opposed to said whole non-aqueous solvent including gamma-butyrolactone and vinylene carbonate ], The rate of propylene carbonate, gamma-butyrolactone, and vinylene carbonate, respectively x (volume %), It is the nonaqueous electrolyte rechargeable battery characterized by said x, said y, said z, and said w filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0.05 \leq w \leq 5$ , respectively when referred to as y (volume %), z (volume %), and w (volume %).

[Claim 16] Thickness is contained in a sheathing material 0.3mm or less and said sheathing material. A lithium ion Occlusion, the positive electrode to emit, and a negative electrode, The separator arranged between said positive electrode in said sheathing material, and said negative electrode, In the nonaqueous electrolyte rechargeable battery possessing the liquefied nonaqueous electrolyte containing the lithium salt which it sinks into said separator at least, and is dissolved in a non-aqueous solvent and said non-aqueous solvent said non-aqueous solvent Ethylene carbonate, propylene carbonate, gamma-butyrolactone, and vinylene carbonate are included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone and vinylene carbonate, respectively x (volume %), It is the nonaqueous electrolyte rechargeable battery characterized by said x, said y, said z, and said w filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0.05 \leq w \leq 5$ , respectively when referred to as y (volume %), z (volume %), and w (volume %).

[Claim 17] Thickness is contained in a sheathing material 0.3mm or less and said sheathing material. A lithium ion Occlusion, the positive electrode to emit, and a negative electrode, In the nonaqueous electrolyte rechargeable battery possessing the electrolyte layer containing the lithium salt which is arranged between said positive electrode in said sheathing material, and said negative electrode, and is dissolved in a non-aqueous solvent and said non-aqueous solvent Said non-aqueous solvent Ethylene carbonate, propylene carbonate, Ethylene carbonate [ as opposed to said whole non-aqueous solvent including gamma-butyrolactone and vinylene carbonate ], The rate of propylene carbonate, gamma-butyrolactone, and vinylene carbonate, respectively x (volume %), It is the nonaqueous electrolyte rechargeable battery characterized by said x, said y, said z, and said w filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0.05 \leq w \leq 5$ , respectively when referred to as y (volume %), z (volume %), and w (volume %).

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to nonaqueous electrolyte and a nonaqueous electrolyte rechargeable battery.

[0002]

[Description of the Prior Art] The rechargeable lithium-ion battery is commercialized as a nonaqueous electrolyte rechargeable battery for pocket devices, such as current and a cellular phone. Porous membrane is used for the organic solvent and separator with

which this cell dissolved the graphite ingredient and the carbonaceous ingredient in lithium cobalt oxide ( $\text{LiCoO}_2$ ) and a negative electrode, and dissolved lithium salt in the positive electrode at nonaqueous electrolyte. As a solvent of said electrolytic solution, the non-aqueous solvent of hypoviscosity and a low-boiling point is used.

[0003] For example, the mixed solvent which consists of propylene carbonate, ethylene carbonate, and gamma-butyrolactone is made into a subject, and the nonaqueous electrolyte rechargeable battery equipped with the electrolytic solution whose ratio of gamma-butyrolactone is ten to 50 volume [ of the whole solvent ] % is indicated by JP,4-14769,A. In this official report, by adding gamma-butyrolactone to the mixed solvent of propylene carbonate and ethylene carbonate, the conductivity of the electrolytic solution in low temperature was raised, and the low-temperature discharge property of a cylindrical shape nonaqueous electrolyte rechargeable battery is improved.

[0004] However, a lot of gas occurs from a negative electrode at the time of an initial charge, or the oxidative degradation of nonaqueous electrolyte produces [ a positive electrode and nonaqueous electrolyte ] the rechargeable lithium-ion battery equipped with the nonaqueous electrolyte indicated by JP,4-14769,A mentioned above in response to the time of storing in an elevated temperature 60 degrees C or more, and the generation of gas breaks out. Therefore, if thickness of the sheathing material by which a positive electrode, a negative electrode, a separator, and nonaqueous electrolyte are contained is made thin in order to make thickness of a cell thin, a sheathing material will blister by the gas which occurred and the trouble of deforming will be produced. When a sheathing material deforms, a cell stops restoring to electronic equipment, and there is a possibility of causing incorrect actuation of electronic equipment. Furthermore, self-discharge tends to progress under hot environments, and, moreover, the cycle-life property of this rechargeable lithium-ion battery is not enough, either.

[0005] On the other hand, controlling that oxidative degradation of the positive electrode which contains a lithium cobalt multiple oxide as an active material is carried out by nonaqueous electrolyte is indicated by JP,11-97062,A by using as nonaqueous electrolyte what dissolved lithium fluoride ( $\text{LiBF}_4$ ) in the solvent whose ratio of gamma-butyrolactone is 100 volume %.

[0006] Moreover, the lithium ion polymer rechargeable battery which equipped 23 pages of the collection (March 28, Heisei 12 issue) of the 67th time convention lecture summaries of the Electrochemical Society of Japan with the polymer gel electrolyte which mixed ethylene carbonate and gamma-butyrolactone so that it might be set to 2:3 by the volume ratio, carried out the polymerization of the electrolytic solution which dissolved  $\text{LiBF}_4$  or  $\text{LiPF}_6$  in the obtained solvent as an electrolyte salt, and the mixed liquor of a polyfunctional acrylate monomer, and was obtained by carrying out chemistry bridge formation is reported.

[0007] However, the nonaqueous electrolyte which dissolved  $\text{LiBF}_4$  in the solvent whose ratio of gamma-butyrolactone is 100 volume %, and the electrolytic solution which dissolved  $\text{LiBF}_4$  or  $\text{LiPF}_6$  in the solvent which mixed ethylene carbonate and gamma-butyrolactone so that it might be set to 2:3 by the volume ratio, and was obtained as an electrolyte salt react with a negative electrode, and reduction decomposition tends to produce it. Consequently, since it becomes easy to produce current concentration in a negative electrode, a lithium metal deposits, or the impedance of a negative-electrode interface becomes high, the charge-and-discharge effectiveness of a negative electrode

falls to a negative-electrode front face, and the fall of a charge-and-discharge cycle property is caused.

[0008]

[Problem(s) to be Solved by the Invention] This invention aims at offering the nonaqueous electrolyte which it can stop that control the generation of gas at the time of storing at an elevated temperature, and a sheathing material blisters, and the self-discharge under hot environments can be controlled, and can be improved in a charge-and-discharge cycle property, and a nonaqueous electrolyte rechargeable battery.

[0009]

[Means for Solving the Problem] In the nonaqueous electrolyte possessing the lithium salt by which the 1st nonaqueous electrolyte concerning this invention is dissolved in a non-aqueous solvent and said non-aqueous solvent said non-aqueous solvent Ethylene carbonate, propylene carbonate, and gamma-butyrolactone, Ethylene carbonate [ as opposed to said whole non-aqueous solvent including the 4th component except said ], The rate of propylene carbonate, gamma-butyrolactone, and said 4th component, respectively x (volume %), When referred to as y (volume %), z (volume %), and p (volume %), said x, said y, said z, and said p are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0 < p \leq 5$ , respectively.

[0010] In the nonaqueous electrolyte possessing the lithium salt by which the 2nd nonaqueous electrolyte concerning this invention is dissolved in a non-aqueous solvent and said non-aqueous solvent said non-aqueous solvent Ethylene carbonate, propylene carbonate, and gamma-butyrolactone, Vinylene carbonate, vinyl ethylene carbonate, an ethylene ape fight, The 4th component which consists of one or more kinds of solvents chosen from the group which consists of phenylethylene carbonate, 12-crown -4, and tetraethylene glycol wood ether is included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone and said 4th component, respectively x (volume %), When referred to as y (volume %), z (volume %), and p (volume %), said x, said y, said z, and said p are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0 < p \leq 5$ , respectively.

[0011] In the 1st and 2nd nonaqueous electrolyte concerning this invention said said x, said y, z, and Above p It is desirable respectively to fill  $15 \leq x \leq 50$ ,  $2 \leq y \leq 30$ ,  $35 \leq z \leq 85$ , and  $0 < p \leq 5$ , and more desirable range is  $20 \leq x \leq 50$ ,  $2 \leq y \leq 25$ ,  $35 \leq z \leq 75$ , and  $0 < p \leq 4$ . Still more desirable range is  $20 \leq x \leq 40$ ,  $2 \leq y \leq 20$ ,  $55 \leq z \leq 75$ , and  $0 < p \leq 3$ .

[0012] In the nonaqueous electrolyte possessing the lithium salt by which the 3rd nonaqueous electrolyte concerning this invention is dissolved in a non-aqueous solvent and said non-aqueous solvent said non-aqueous solvent Ethylene carbonate, propylene carbonate, and gamma-butyrolactone, Ethylene carbonate [ as opposed to said whole non-aqueous solvent including vinylene carbonate and the 5th component except said ], The rate of propylene carbonate, gamma-butyrolactone, vinylene carbonate, and said 5th component, respectively x (volume %), When referred to as y (volume %), z (volume %), w (volume %), and q (volume %), said x, said y, said z, said w, and said q are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ ,  $0 < w \leq 5$ , and  $0 < q \leq 5$ , respectively.

[0013] In the nonaqueous electrolyte possessing the lithium salt by which the 4th nonaqueous electrolyte concerning this invention is dissolved in a non-aqueous solvent



and said non-aqueous solvent said non-aqueous solvent Ethylene carbonate, propylene carbonate, and gamma-butyrolactone, Vinylene carbonate, vinyl ethylene carbonate, an ethylene azeotrope, The 5th component which consists of one or more kinds of solvents chosen from the group which consists of phenylethylene carbonate, 12-crown -4, and tetraethylene glycol wood ether is included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone, vinylene carbonate, and said 5th component, respectively x (volume %), When referred to as y (volume %), z (volume %), w (volume %), and q (volume %), said x, said y, said z, said w, and said q are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ ,  $0 < w \leq 5$ , and  $0 < q \leq 5$ , respectively.

[0014] In the 3rd and 4th nonaqueous electrolyte concerning this invention said x, said y, said z, Above w, and said q It is desirable respectively to fill  $15 \leq x \leq 50$ ,  $2 \leq y \leq 30$ ,  $35 \leq z \leq 85$ ,  $0 < w \leq 5$ , and  $0 < q \leq 5$ , and more desirable range is  $20 \leq x \leq 50$ ,  $2 \leq y \leq 25$ ,  $35 \leq z \leq 75$ ,  $0 < w \leq 3$ , and  $0 < q \leq 4$ . Still more desirable range is  $20 \leq x \leq 40$ ,  $2 \leq y \leq 20$ ,  $55 \leq z \leq 75$ ,  $0 < w \leq 2$ , and  $0 < q \leq 3$ .

[0015] The 5th nonaqueous electrolyte concerning this invention possesses a non-aqueous solvent and the lithium salt dissolved in said non-aqueous solvent. Said non-aqueous solvent Ethylene carbonate, propylene carbonate, gamma-butyrolactone, and vinylene carbonate are included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone and vinylene carbonate, respectively x (volume %), When referred to as y (volume %), z (volume %), and w (volume %), said x, said y, said z, and said w are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0.05 \leq w \leq 5$ , respectively.

[0016] In the 5th nonaqueous electrolyte concerning this invention said said x, said y, z, and Above w It is desirable respectively to fill  $15 \leq x \leq 50$ ,  $2 \leq y \leq 30$ ,  $35 \leq z \leq 85$ , and  $0.05 \leq w \leq 5$ , and more desirable range is  $20 \leq x \leq 50$ ,  $2 \leq y \leq 25$ ,  $35 \leq z \leq 75$ , and  $0.1 \leq w \leq 3$ . Still more desirable range is  $20 \leq x \leq 40$ ,  $3 \leq y \leq 20$ ,  $55 \leq z \leq 75$ , and  $0.2 \leq w \leq 2$ .

[0017] Thickness the 1st nonaqueous electrolyte rechargeable battery concerning this invention A sheathing material 0.3mm or less, In the nonaqueous electrolyte rechargeable battery possessing the electrode group contained in said sheathing material, and the nonaqueous electrolyte containing the lithium salt which is held at said electrode group and dissolved in a non-aqueous solvent and said non-aqueous solvent Said non-aqueous solvent Ethylene carbonate and propylene carbonate, Ethylene carbonate [ as opposed to said whole non-aqueous solvent including gamma-butyrolactone and the 4th component except said ], The rate of propylene carbonate, gamma-butyrolactone, and said 4th component, respectively x (volume %), When referred to as y (volume %), z (volume %), and p (volume %), said x, said y, said z, and said p are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0 < p \leq 5$ , respectively.

[0018] Thickness the 2nd nonaqueous electrolyte rechargeable battery concerning this invention A sheathing material 0.3mm or less, In the nonaqueous electrolyte rechargeable battery possessing the electrode group contained in said sheathing material, and the nonaqueous electrolyte containing the lithium salt which is held at said electrode group and dissolved in a non-aqueous solvent and said non-aqueous solvent Said non-aqueous solvent Ethylene carbonate and propylene carbonate, Gamma-butyrolactone, and vinylene carbonate, vinyl ethylene carbonate, The 4th component which consists of one

or more kinds of solvents chosen from the group which consists of an ethylene azeotrope, phenylethylene carbonate, 12-crown -4, and tetraethylene glycol wood ether is included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone and said 4th component, respectively x (volume %), When referred to as y (volume %), z (volume %), and p (volume %), said x, said y, said z, and said p are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0 < p \leq 5$ , respectively.

[0019] Thickness the 3rd nonaqueous electrolyte rechargeable battery concerning this invention A sheathing material 0.3mm or less, It is arranged between the positive electrode and negative electrode which are contained in said sheathing material, and said positive electrode in said sheathing material and said negative electrode. In the nonaqueous electrolyte rechargeable battery possessing the electrolyte layer containing the polymer which has the function to make nonaqueous electrolyte and said nonaqueous electrolyte gel said nonaqueous electrolyte The lithium salt dissolved in a non-aqueous solvent and said non-aqueous solvent is included. Said non-aqueous solvent Ethylene carbonate, propylene carbonate, and gamma-butyrolactone, Ethylene carbonate [ as opposed to said whole non-aqueous solvent including the 4th component except said ], The rate of propylene carbonate, gamma-butyrolactone, and said 4th component, respectively x (volume %), When referred to as y (volume %), z (volume %), and p (volume %), said x, said y, said z, and said p are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0 < p \leq 5$ , respectively.

[0020] Thickness the 4th nonaqueous electrolyte rechargeable battery concerning this invention A sheathing material 0.3mm or less, It is arranged between the positive electrode and negative electrode which are contained in said sheathing material, and said positive electrode in said sheathing material and said negative electrode. In the nonaqueous electrolyte rechargeable battery possessing the electrolyte layer containing the polymer which has the function to make nonaqueous electrolyte and said nonaqueous electrolyte gel said nonaqueous electrolyte The lithium salt dissolved in a non-aqueous solvent and said non-aqueous solvent is included. Said non-aqueous solvent Ethylene carbonate, propylene carbonate, and gamma-butyrolactone, Vinylene carbonate, vinyl ethylene carbonate, an ethylene azeotrope, The 4th component which consists of one or more kinds of solvents chosen from the group which consists of phenylethylene carbonate, 12-crown -4, and tetraethylene glycol wood ether is included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone and said 4th component, respectively x (volume %), When referred to as y (volume %), z (volume %), and p (volume %), said x, said y, said z, and said p are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0 < p \leq 5$ , respectively.

[0021] In the 4th nonaqueous electrolyte rechargeable battery the 1- concerning this invention -- said x, said y, said z, and said p It is desirable respectively to fill  $15 \leq x \leq 50$ ,  $2 \leq y \leq 30$ ,  $35 \leq z \leq 85$ , and  $0 < p \leq 5$ , and more desirable range is  $20 \leq x \leq 50$ ,  $2 \leq y \leq 25$ ,  $35 \leq z \leq 75$ , and  $0 < p \leq 4$ . Still more desirable range is  $20 \leq x \leq 40$ ,  $2 \leq y \leq 20$ ,  $55 \leq z \leq 75$ , and  $0 < p \leq 3$ .

[0022] Thickness the 5th nonaqueous electrolyte rechargeable battery concerning this invention A sheathing material 0.3mm or less, In the nonaqueous electrolyte rechargeable battery possessing the electrode group contained in said sheathing material, and the nonaqueous electrolyte containing the lithium salt which is held at said electrode group and dissolved in a non-aqueous solvent and said non-aqueous solvent Said non-aqueous

solvent Ethylene carbonate and propylene carbonate, Gamma-butyrolactone, vinylene carbonate, and the 5th component except said are included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone, vinylene carbonate, and said 5th component, respectively x (volume %), When referred to as y (volume %), z (volume %), w (volume %), and q (volume %), said x, said y, said z, said w, and said q are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ ,  $0 < w \leq 5$ , and  $0 < q \leq 5$ , respectively.

[0023] Thickness the 6th nonaqueous electrolyte rechargeable battery concerning this invention A sheathing material 0.3mm or less, In the nonaqueous electrolyte rechargeable battery possessing the electrode group contained in said sheathing material, and the nonaqueous electrolyte containing the lithium salt which is held at said electrode group and dissolved in a non-aqueous solvent and said non-aqueous solvent Said non-aqueous solvent Ethylene carbonate and propylene carbonate, Gamma-butyrolactone, vinylene carbonate, and vinyl ethylene carbonate, The 5th component which consists of one or more kinds of solvents chosen from the group which consists of an ethylene ape fight, phenylethylene carbonate, 12-crown -4, and tetraethylene glycol wood ether is included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone, vinylene carbonate, and said 5th component, respectively x (volume %), When referred to as y (volume %), z (volume %), w (volume %), and q (volume %), said x, said y, said z, said w, and said q are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ ,  $0 < w \leq 5$ , and  $0 < q \leq 5$ , respectively.

[0024] Thickness the 7th nonaqueous electrolyte rechargeable battery concerning this invention A sheathing material 0.3mm or less, It is arranged between the positive electrode and negative electrode which are contained in said sheathing material, and said positive electrode in said sheathing material and said negative electrode. In the nonaqueous electrolyte rechargeable battery possessing the electrolyte layer containing the polymer which has the function to make nonaqueous electrolyte and said nonaqueous electrolyte gel said nonaqueous electrolyte The lithium salt dissolved in a non-aqueous solvent and said non-aqueous solvent is included. Said non-aqueous solvent Ethylene carbonate, propylene carbonate, and gamma-butyrolactone, Ethylene carbonate [ as opposed to said whole non-aqueous solvent including vinylene carbonate and the 5th component except said ], The rate of propylene carbonate, gamma-butyrolactone, vinylene carbonate, and said 5th component, respectively x (volume %), When referred to as y (volume %), z (volume %), w (volume %), and q (volume %), said x, said y, said z, said w, and said q are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ ,  $0 < w \leq 5$ , and  $0 < q \leq 5$ , respectively.

[0025] Thickness the 8th nonaqueous electrolyte rechargeable battery concerning this invention A sheathing material 0.3mm or less, It is arranged between the positive electrode and negative electrode which are contained in said sheathing material, and said positive electrode in said sheathing material and said negative electrode. In the nonaqueous electrolyte rechargeable battery possessing the electrolyte layer containing the polymer which has the function to make nonaqueous electrolyte and said nonaqueous electrolyte gel said nonaqueous electrolyte The lithium salt dissolved in a non-aqueous solvent and said non-aqueous solvent is included. Said non-aqueous solvent Ethylene carbonate, propylene carbonate, and gamma-butyrolactone, Vinylene carbonate, vinyl ethylene carbonate, an ethylene ape fight, The 5th component which consists of one or

more kinds of solvents chosen from the group which consists of phenylethylene carbonate, 12-crown -4, and tetraethylene glycol wood ether is included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone, vinylene carbonate, and said 5th component, respectively x (volume %), When referred to as y (volume %), z (volume %), w (volume %), and q (volume %), In the 8th nonaqueous electrolyte rechargeable battery the 5- concerning this invention characterized by said x, said y, said z, said w, and said q filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ ,  $0 < w \leq 5$ , and  $0 < q \leq 5$ , respectively -- Said x, said y, said z, Above w, and said q It is desirable respectively to fill  $15 \leq x \leq 50$ ,  $2 \leq y \leq 30$ ,  $35 \leq z \leq 85$ ,  $0 < w \leq 5$ , and  $0 < q \leq 5$ , and more desirable range is  $20 \leq x \leq 50$ ,  $2 \leq y \leq 25$ ,  $35 \leq z \leq 75$ ,  $0 < w \leq 3$ , and  $0 < q \leq 4$ . Still more desirable range is  $20 \leq x \leq 40$ ,  $2 \leq y \leq 20$ ,  $55 \leq z \leq 75$ ,  $0 < w \leq 2$ , and  $0 < q \leq 3$ .

[0026] Thickness the 9th nonaqueous electrolyte rechargeable battery concerning this invention A sheathing material 0.3mm or less, In the nonaqueous electrolyte rechargeable battery possessing the electrode group contained in said sheathing material, and the nonaqueous electrolyte containing the lithium salt which is held at said electrode group and dissolved in a non-aqueous solvent and said non-aqueous solvent Said non-aqueous solvent Ethylene carbonate, propylene carbonate, Ethylene carbonate [ as opposed to said whole non-aqueous solvent including gamma-butyrolactone and vinylene carbonate ], The rate of propylene carbonate, gamma-butyrolactone, and vinylene carbonate, respectively x (volume %), When referred to as y (volume %), z (volume %), and w (volume %), said x, said y, said z, and said w are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0.05 \leq w \leq 5$ , respectively.

[0027] The 10th nonaqueous electrolyte rechargeable battery concerning this invention Thickness is contained in a sheathing material 0.3mm or less and said sheathing material. A lithium ion Occlusion, the positive electrode to emit, and a negative electrode, The separator arranged between said positive electrode in said sheathing material, and said negative electrode, In the nonaqueous electrolyte rechargeable battery possessing the liquefied nonaqueous electrolyte containing the lithium salt which it sinks into said separator at least, and is dissolved in a non-aqueous solvent and said non-aqueous solvent said non-aqueous solvent Ethylene carbonate, propylene carbonate, gamma-butyrolactone, and vinylene carbonate are included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone and vinylene carbonate, respectively x (volume %), When referred to as y (volume %), z (volume %), and w (volume %), said x, said y, said z, and said w are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0.05 \leq w \leq 5$ , respectively.

[0028] The 11th nonaqueous electrolyte rechargeable battery concerning this invention Thickness is contained in a sheathing material 0.3mm or less and said sheathing material. A lithium ion Occlusion, the positive electrode to emit, and a negative electrode, In the nonaqueous electrolyte rechargeable battery possessing the electrolyte layer containing the lithium salt which is arranged between said positive electrode in said sheathing material, and said negative electrode, and is dissolved in a non-aqueous solvent and said non-aqueous solvent Said non-aqueous solvent Ethylene carbonate, propylene carbonate, Ethylene carbonate [ as opposed to said whole non-aqueous solvent including gamma-butyrolactone and vinylene carbonate ], The rate of propylene carbonate, gamma-butyrolactone, and vinylene carbonate, respectively x (volume %), When referred to as y

(volume %), z (volume %), and w (volume %), said x, said y, said z, and said w are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0.05 \leq w \leq 5$ , respectively.

[0029] In the 11th nonaqueous electrolyte rechargeable battery the 9- concerning this invention -- said x, said y, said z, and said w It is desirable respectively to fill  $15 \leq x \leq 50$ ,  $2 \leq y \leq 30$ ,  $35 \leq z \leq 85$ , and  $0.05 \leq w \leq 5$ , and more desirable range is  $20 \leq x \leq 50$ ,  $2 \leq y \leq 25$ ,  $35 \leq z \leq 75$ , and  $0.1 \leq w \leq 3$ . Still more desirable range is  $20 \leq x \leq 40$ ,  $3 \leq y \leq 20$ ,  $55 \leq z \leq 75$ , and  $0.2 \leq w \leq 2$ .

[0030] the 1- concerning this invention -- as for said negative electrode, in the 11th nonaqueous electrolyte rechargeable battery, it is desirable that occlusion and the carbonaceous object to emit are included for a lithium ion.

[0031] moreover, the 1- concerning this invention -- as for said carbonaceous object, in the 11th nonaqueous electrolyte rechargeable battery, it is desirable to include a mesophase pitch based carbon fiber.

[0032]

[Embodiment of the Invention] Thickness is held at a sheathing material 0.3mm or less, the electrode group contained in said sheathing material, and said electrode group, and, as for the nonaqueous electrolyte rechargeable battery concerning this invention, possesses the nonaqueous electrolyte containing the lithium salt dissolved in a non-aqueous solvent and said non-aqueous solvent.

[0033] Either of for example, (A) - (C) explained below is used for said non-aqueous solvent.

[0034] (A) a non-aqueous solvent A -- this non-aqueous solvent A with ethylene carbonate and propylene carbonate Gamma-butyrolactone, and vinylene carbonate, vinyl ethylene carbonate, The 4th component which consists of one or more kinds of solvents chosen from the group which consists of an ethylene ape fight, phenylethylene carbonate, 12-crown -4, and tetraethylene glycol wood ether is included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, When the rate of gamma-butyrolactone and said 4th component is set to x (volume %), and y (volume %), z (volume %) and p (volume %), respectively, said x, said y, said z, and said p fill  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0 < p \leq 5$ , respectively.

[0035] (B) a non-aqueous solvent B -- this non-aqueous solvent B -- ethylene carbonate and propylene carbonate -- Ethylene carbonate [ as opposed to said whole non-aqueous solvent including gamma-butyrolactone and vinylene carbonate ], The rate of propylene carbonate, gamma-butyrolactone, and vinylene carbonate, respectively x (volume %), When referred to as y (volume %), z (volume %), and w (volume %), said x, said y, said z, and said w fill  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0.05 \leq w \leq 5$ , respectively.

[0036] (C) a non-aqueous solvent C -- this non-aqueous solvent C with ethylene carbonate and propylene carbonate Gamma-butyrolactone, vinylene carbonate, and vinyl ethylene carbonate, The 5th component which consists of one or more kinds of solvents chosen from the group which consists of an ethylene ape fight, phenylethylene carbonate, 12-crown -4, and tetraethylene glycol wood ether is included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, The rate of gamma-butyrolactone, vinylene carbonate, and said 5th component, respectively x (volume %), When referred to as y (volume %), z (volume %), w (volume %), and q (volume %), said x, said y, said z, said w, and said q fill  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ ,  $0 < w \leq 5$ ,

and  $0 < q \leq 5$ , respectively.

[0037] What has the gestalt of liquefied or gel can be used for said nonaqueous electrolyte. Especially, liquefied nonaqueous electrolyte is desirable. Since ionic conductivity can be made high by using liquefied nonaqueous electrolyte, interfacial resistance of a negative electrode and a separator can be made small at the interfacial resistance list of a positive electrode and a separator.

[0038] Said nonaqueous electrolyte is prepared by the approach explained to the following (I) - (IV).

[0039] (I) Nonaqueous electrolyte is obtained by dissolving lithium salt in either of non-aqueous-solvent A-C mentioned above (liquefied nonaqueous electrolyte).

[0040] (II) It is made to dry after forming the paste prepared by mixing either of non-aqueous-solvent A-C mentioned above, lithium salt, and a polymer. The obtained thin film is made to intervene between a positive electrode and a negative electrode, and an electrode group is produced. After infiltrating liquefied nonaqueous electrolyte into this electrode group, said thin film is made to plasticize under reduced pressure.

[0041] (III) After infiltrating into a separator the slurry containing either of non-aqueous-solvent A-C mentioned above, lithium salt, and a gelling agent, said separator is made to intervene between a positive electrode and a negative electrode, and the electrode group holding gel nonaqueous electrolyte is obtained.

[0042] (IV) The slurry containing either of non-aqueous-solvent A-C mentioned above, lithium salt, and a gelling agent is applied to a positive electrode or a negative electrode, and the electrode group holding gel nonaqueous electrolyte is obtained by making a separator intervene between this forward negative electrode.

[0043] As said gelling agent, a polyacrylonitrile (PAN) can be mentioned, for example.

[0044] Hereafter, the example (a nonaqueous electrolyte rechargeable battery (I) and nonaqueous electrolyte rechargeable battery (II)) of the rechargeable battery concerning this invention is explained.

[0045] 1. Nonaqueous Electrolyte Rechargeable Battery (I)

Thickness is contained in a sheathing material 0.3mm or less and said sheathing material, it sinks into said separator at least with the electrode group to which the separator intervened the lithium ion between occlusion, the positive electrode to emit, and the negative electrode, and this nonaqueous electrolyte rechargeable battery possesses the liquefied nonaqueous electrolyte (nonaqueous electrolyte) containing the lithium salt dissolved in a non-aqueous solvent and said non-aqueous solvent.

[0046] Said electrode group, a positive electrode, a negative electrode, a separator, nonaqueous electrolyte, and a sheathing material are explained.

[0047] 1) By the electrode group of electrode \*\*\*\*, it is desirable that the positive electrode, the negative electrode, and the separator are unified. This electrode group is produced by the approach explained to the following (i) - (ii).

[0048] (i) After making a separator intervene between them, winding a positive electrode and a negative electrode around a flat configuration, or making a separator intervene between them and winding a positive electrode and a negative electrode around a curled form, it compresses in the direction of a path, or a separator is made to intervene between them and a positive electrode and a negative electrode are bent once or more. By giving hot forming in the direction of a laminating of the obtained flat-like object, carry out heat curing of the binder contained in a positive electrode and a negative electrode, a positive

electrode, a negative electrode, and a separator are made to unify, and an electrode group is obtained.

[0049] After said hot forming contains a flat-like object to a sheathing material, it may be performed, and before containing to a sheathing material, it may be performed.

[0050] As for the ambient atmosphere which performs hot forming, it is desirable to make it a reduced pressure ambient atmosphere including a vacuum or an ordinary pressure ambient atmosphere.

[0051] The insert lump by press forming or the die etc. can perform shaping.

[0052] As for the temperature of said hot forming, it is desirable to carry out within the limits of 40-120 degrees C. The more desirable range is 60-100 degrees C.

[0053] As for the moulding pressure of said hot forming, it is desirable to carry out within the limits of 0.01-20kg/cm<sup>2</sup>. The still more desirable range is 8-15kg/cm<sup>2</sup>.

[0054] (ii) After making a separator intervene between them, winding a positive electrode and a negative electrode around a flat configuration, or making a separator intervene between them and winding a positive electrode and a negative electrode around a curled form, it compresses in the direction of a path, or a separator is made to intervene between them and a positive electrode and a negative electrode are bent once or more. After infiltrating the solution of the macromolecule which has an adhesive property in the obtained flat-like object, the solvent in said solution is evaporated by performing a vacuum drying. Subsequently, by giving hot forming, a positive electrode, a negative electrode, and a separator are made to unify, and an electrode group is obtained. By such electrode group, bond strength can be made high, stopping the internal resistance of a rechargeable battery low, since the negative electrode and the separator are unified with the macromolecule which has the adhesive property with which these interior and boundaries are dotted while the positive electrode and the separator are unified with the macromolecule which has the adhesive property with which these interior and boundaries are dotted.

[0055] After said hot forming contains a flat-like object to a sheathing material, it may be performed, and before containing to a sheathing material, it may be performed.

[0056] The solution of the macromolecule which has said adhesive property is prepared by dissolving an adhesive macromolecule in an organic solvent.

[0057] As for the macromolecule which has said adhesive property, it is desirable that it is what can maintain a high adhesive property where nonaqueous electrolyte is held. Furthermore, when this giant molecule has high lithium ion conductivity, in addition, it is desirable. Specifically, a polyacrylonitrile (PAN), polyacrylate (PMMA), polyvinylidene fluoride (PVdF), a polyvinyl chloride (PVC), or polyethylene oxide (PEO) can be mentioned. Especially, polyvinylidene fluoride is desirable. Polyvinylidene fluoride can hold nonaqueous electrolyte, and since it will produce gelation in part if it contains nonaqueous electrolyte, it can improve ionic conductivity more.

[0058] The range where it is desirable still more desirable that the boiling point of said solvent is 200 degrees C or less is 180 degrees C or less. The lower limit with desirable still more desirable making the lower limit of the boiling point into 50 degrees C is 100 degrees C.

[0059] As for the concentration of the macromolecule which has an adhesive property in said solution, it is desirable to make it 0.05 - 2.5% of the weight of the range. The more desirable range of concentration is 0.1 - 1.5 % of the weight.

[0060] When the concentration of the macromolecule which has the adhesive property of said solution is 0.05 - 2.5 % of the weight, as for the injection rate of said solution, it is desirable to make it the range which is 0.1-2ml per cell capacity 100mAh. The more desirable range of said injection rate is 0.15-1ml per cell capacity 100mAh.

[0061] As for said vacuum drying, it is desirable to carry out below 100 degrees C. More desirable vacuum-drying temperature is 40-100 degrees C.

[0062] As for the total amount of the macromolecule which has the adhesive property included in said cell, it is desirable to make it 0.1-6mg per cell capacity 100mAh. The more desirable range of the total amount of the macromolecule which has an adhesive property is 0.2-1mg per cell capacity 100mAh.

[0063] 2) \*\*\*\* -- this positive electrode has the structure where the positive-electrode layer containing an active material was supported by one side or both sides of a charge collector.

[0064] Said positive-electrode layer contains positive active material, a binder, and an electric conduction agent.

[0065] As said positive active material, chalcogen compounds, such as various oxide, for example, a manganese dioxide, a lithium manganese multiple oxide, a lithium content nickel oxide, lithium content cobalt oxide, lithium content nickel cobalt oxide, a lithium content ferric acid ghost, a banazin san ghost containing a lithium, and 2 titanium sulfides, molybdenum disulfide, etc. can be mentioned. Especially, when lithium content cobalt oxide (for example,  $\text{LiCoO}_2$ ), lithium content nickel cobalt oxide (for example,  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ ), and a lithium manganese multiple oxide (for example,  $\text{LiMn}_2\text{O}_4$  and  $\text{LiMnO}_2$ ) are used, since the high voltage is obtained, it is desirable.

[0066] As said electric conduction agent, acetylene black, carbon black, a graphite, etc. can be mentioned, for example.

[0067] Said binder has the function which is made to hold an active material to a charge collector, and connects active materials. As said binder, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVdF), an ethylene-propylene-diene copolymer (EPDM), a styrene butadiene rubber (SBR), etc. can be used, for example.

[0068] the blending ratio of coal of said positive active material, an electric conduction agent, and a binder -- 80 - 95 % of the weight of positive active material, and an electric conduction agent -- it is desirable to make it the range of 2 - 7 % of the weight of binders three to 20% of the weight.

[0069] As said charge collector, the conductive substrate of a vesicular structure or a nonporous conductive substrate can be used. These conductivity substrate can be formed from aluminum, stainless steel, or nickel.

[0070] Especially, a hole with a diameter of 3mm or less is 2 10cm. It is desirable to use the conductive substrate which has the two-dimensional vesicular structure which exists at a rate of one or more hits. As for the diameter of a hole, it is more desirable to make it the range of 0.1-1mm. Moreover, the abundance of a hole is 2 10cm. It is more desirable to make it the range of 10-20 hits.

[0071] A hole with a diameter of 3mm or less mentioned above is 2 10cm. As for the conductive substrate which has the two-dimensional vesicular structure which exists at a rate of one or more hits, it is desirable to make thickness into the range of 15-100 micrometers. The more desirable range of thickness is 30-80 micrometers.

[0072] Said positive electrode suspends an electric conduction agent and a binder in



positive active material at a suitable solvent, and is produced by applying this suspended solid to a charge collector, drying, and making it the shape of sheet metal.

[0073] Moreover, when it produces by the approach explained to (ii) which mentioned said electrode group above, said positive electrode contains further the macromolecule which has an adhesive property.

[0074] 3) The negative-electrode aforementioned negative electrode has the structure where the negative-electrode layer was supported by one side or both sides of a charge collector.

[0075] Said negative-electrode layer contains occlusion, the carbonaceous object to emit, and a binder for a lithium ion.

[0076] A graphite ingredient or a carbonaceous ingredient obtained as said carbonaceous object by heat-treating at 500-3000 degrees C to graphite ingredients, such as a graphite, corks, a carbon fiber, and spherical carbon, or a carbonaceous ingredient, thermosetting resin, an isotropic pitch, a mesophase pitch, a mesophase pitch based carbon fiber, a mesophase microsphere, etc. (a mesophase pitch based carbon fiber becoming high and having capacity and an especially desirable charge-and-discharge cycle property) can be mentioned. Especially, it is obtained by making temperature of said heat treatment into 2000 degrees C or more, and is the spacing d002 of a field (002). It is desirable to use the graphite ingredient which has the graphite crystal which is 0.34nm or less. The nonaqueous electrolyte rechargeable battery equipped with the negative electrode which contains such a graphite ingredient as a carbonaceous object can improve sharply cell capacity and a high current discharge property. Said spacing d002 It is still more desirable that it is 0.336nm or less.

[0077] As said binder, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVdF), an ethylene-propylene-diene copolymer (EPDM), styrene-PUTAJI en rubber (SBR), a carboxymethyl cellulose (CMC), etc. can be used, for example.

[0078] As for the blending ratio of coal of said carbonaceous object and said binder, it is desirable that it is the range of 90 - 98 % of the weight of carbonaceous objects and 2 - 20 % of the weight of binders.

[0079] As said charge collector, the conductive substrate of a vesicular structure or a nonporous conductive substrate can be used. These conductivity substrate can be formed from copper, stainless steel, or nickel.

[0080] Especially, a hole with a diameter of 3mm or less is 2 10cm. It is desirable to use the conductive substrate which has the two-dimensional vesicular structure which exists at a rate of one or more hits. As for the diameter of a hole, it is more desirable to make it the range of 0.1-1mm. Moreover, the abundance of a hole is 2 10cm. It is more desirable to make it the range of 10-20 hits.

[0081] A hole with a diameter of 3mm or less mentioned above is 2 10cm. As for the conductive substrate which has the two-dimensional vesicular structure which exists at a rate of one or more hits, it is desirable to make thickness into the range of 10-50 micrometers.

[0082] Said negative electrode applies the suspended solid which kneaded the lithium ion under existence of a solvent and was obtained [ lithium ion ] in occlusion, the carbonaceous object to emit, and the binder to a charge collector, and after drying, it is produced by pressing or 2 - 5 times multistage story pressing once by the desired pressure.

[0083] Moreover, when it produces by the approach explained to (ii) which mentioned

said electrode group above, said negative electrode contains further the macromolecule which has an adhesive property.

[0084] although said negative-electrode layer contains occlusion and the carbon matter to emit for the lithium ion mentioned above -- others -- metals, such as aluminum, magnesium, tin, and a silicon, a metallic oxide, and metallic sulfide -- or the metallic compounds chosen from a metal nitride and a lithium alloy may be included.

[0085] As said metallic oxide, a stannic-acid ghost, silicon oxide, a lithium titanate-acid ghost, a niobic acid ghost, a tungstic-acid ghost, etc. can be mentioned, for example.

[0086] As said metallic sulfide, a tin sulfide, a titanium sulfide, etc. can be mentioned, for example.

[0087] As said metal nitride, a lithium cobalt nitride, a lithium iron nitride, a lithium manganese nitride, etc. can be mentioned, for example.

[0088] As said lithium alloy, a lithium aluminium alloy, a lithium tin alloy, a lithium lead alloy, a lithium silicon alloy, etc. can be mentioned, for example.

[0089] 4) The separator of separator \*\* is formed from a porosity sheet.

[0090] As said porosity sheet, a porosity film or a nonwoven fabric can be used, for example. As for said porosity sheet, it is desirable to consist of at least one kind of ingredient chosen from polyolefine and a cellulose. As said polyolefine, polyethylene and polypropylene can be mentioned, for example. Since the porosity film which consists of polyethylene, polypropylene, or both especially can improve the safety of a rechargeable battery, it is desirable.

[0091] The range where it is desirable still more desirable setting thickness of said porosity sheet to 30 micrometers or less is 25 micrometers or less. Moreover, the lower limit with desirable still more desirable setting the lower limit of thickness to 5 micrometers is 8 micrometers.

[0092] As for said porosity sheet, it is desirable that it is 20% or less about 120 degrees C and the rate of a heat shrink in 1 hour. As for said rate of a heat shrink, it is more desirable to make it to 15% or less.

[0093] As for said porosity sheet, it is desirable that it is the range whose porosity is 30 - 60%. The more desirable range of porosity is 35 - 50%.

[0094] For said porosity sheet, air permeability is 600 second / 100cm<sup>3</sup>. It is desirable that it is the following. Air permeability means the time amount (second) taken for the air of 3 to penetrate a porosity sheet 100cm. The upper limit of air permeability is 500 second / 100cm<sup>3</sup>. Carrying out is more desirable. moreover, the lower limit of air permeability -- 50 second / 100cm<sup>3</sup> the lower limit with desirable still more desirable carrying out -- 80 second / 100cm<sup>3</sup> it is .

[0095] Moreover, when it produces by the approach explained to (ii) which mentioned said electrode group above, said separator contains further the macromolecule which has an adhesive property.

[0096] 5) Liquefied nonaqueous electrolyte (nonaqueous electrolyte)

This liquefied nonaqueous electrolyte consists of non-aqueous solvents in which lithium salt was dissolved.

[0097] Either of (A) - (C) mentioned above is used for said non-aqueous solvent. First, a non-aqueous solvent A is explained.

[0098] The reason for specifying the rate to the whole non-aqueous solvent of each solvent in said range is explained.

[0099] a. Gamma-butyrolactone (BL)

It is become easy to generate gas at the time of an elevated temperature that the ratio (z) to the whole non-aqueous solvent of BL is under 30 volume %. Moreover, since each of other solvents is annular carbonate, if the ratio of BL is made under into 30 volume %, the ratio of annular carbonate will become high relatively and solvent viscosity will become remarkably high. Consequently, since the conductivity and permeability of nonaqueous electrolyte fall sharply, a charge-and-discharge cycle property and the discharge property under the low-temperature environment near -20 degree C fall. On the other hand, if a ratio exceeds 85 volume %, since the reaction of a negative electrode and BL will arise, a charge-and-discharge cycle property falls. That is, if a negative electrode (for example, thing containing the carbonaceous object which carries out occlusion emission of the lithium ion), and BL react and reduction decomposition of nonaqueous electrolyte arises, the coat which checks a charge-and-discharge reaction on the surface of a negative electrode will be formed. Consequently, since it becomes easy to produce current concentration in a negative electrode, a lithium metal deposits, or the impedance of a negative-electrode interface becomes high, the charge-and-discharge effectiveness of a negative electrode falls to a negative-electrode front face, and the fall of a charge-and-discharge cycle property is caused. A more desirable ratio is 35 volume % - 85 volume %, a still more desirable ratio is below 75 volume % more than 35 volume %, and the most desirable ratio is below 75 volume % more than 55 volume %.

[0100] b. Ethylene carbonate (EC)

Since there is a possibility that it may become difficult to cover a negative-electrode front face by the protective coat when the ratio (x) to the whole non-aqueous solvent of EC is made under into 15 volume %, the reaction of a negative electrode and BL progresses and it becomes difficult to fully improve a charge-and-discharge cycle property. On the other hand, since there is a possibility that the viscosity of nonaqueous electrolyte may become high and ionic conductivity may fall when the ratio of EC exceeds 50 volume %, it becomes difficult to fully improve a charge-and-discharge cycle property and a low-temperature discharge property. The more desirable range of the ratio of EC is below 50 volume % more than 20 volume %, and the still more desirable range is below 40 volume % more than 20 volume %.

[0101] c. Propylene carbonate (PC)

If the ratio (y) to the whole non-aqueous solvent of PC is made under into 2 volume %, it becomes difficult to carry out eburnation of the protective coat on the front face of a negative electrode, the reaction of a negative electrode and BL will progress and it will become difficult to fully improve a charge-and-discharge cycle property and a low-temperature discharge property. On the other hand, if the ratio of PC exceeds 35 volume %, the viscosity of nonaqueous electrolyte will become high and ionic conductivity will fall. Moreover, the generation of gas at the time of elevated-temperature storage and an initial charge becomes remarkable, and it becomes difficult to fully improve a charge-and-discharge cycle property. The more desirable range of the ratio of PC is below 30 volume % more than 2 volume %, the still more desirable range is below 25 volume % more than 2 volume %, and the still more desirable range is below 20 volume % more than 2 volume %. The most desirable range is below 20 volume % more than 3 volume %.

[0102] In addition, PC moves to the front face of said negative electrode from said non-

aqueous solvent into an initial-charge-and-discharge process, and adheres to the front face of said negative electrode. Therefore, in the non-aqueous solvent which exists in the rechargeable battery with which the initial-charge-and-discharge process was given, the rate of PC to the whole non-aqueous solvent decreases from rechargeable battery assembly before. It becomes large, so that the addition of the percentage reduction of PC decreases.

[0103] d. If the ratio (p) to the whole non-aqueous solvent of the 4th component of the 4th component exceeds 5 volume %, there may be a possibility that the generation of gas at the time of elevated-temperature storage and an initial charge may become remarkable, or the coat formed in a negative-electrode front face may become thick, and it may become difficult for the impedance of a negative electrode to increase and to acquire the outstanding charge-and-discharge cycle property and a low-temperature discharge property. Moreover, if the ratio to the whole non-aqueous solvent of the 4th component is made under into 0.05 volume % It becomes difficult for whenever [ precise ], and thickness of the protective coat formed in a negative-electrode front face to be insufficient, and to fully improve a charge-and-discharge cycle property and a low-temperature discharge property, or Or since it may become impossible to control the self-discharge at the time of elevated-temperature storage, as for the ratio to the whole non-aqueous solvent of the 4th component, it is desirable to carry out within the limits of 0.05 volume % - 5 volume %.

[0104] When using vinyl ethylene carbonate (VEC) as the 4th component, the desirable range is 0.05 volume % - 5 volume %, the still more desirable range is 0.1 volume % - 4 volume %, and the most desirable range is 0.2 volume % - 3 volume %.

[0105] When using an ethylene ape fight (ES) as the 4th component, the desirable range is below 5 volume %, the still more desirable range is below 3 volume %, and the most desirable range is below 1.5 volume %.

[0106] When using phenylethylene carbonate (phEC) as the 4th component, the desirable range is below 5 volume %, the still more desirable range is below 4 volume %, and the most desirable range is below 3 volume %.

[0107] When using 12-crown -4 as the 4th component, the desirable range is below 5 volume %, the still more desirable range is below 4 volume %, and the most desirable range is below 3 volume %.

[0108] When using tetraethylene glycol wood ether as the 4th component, the desirable range is below 5 volume %, the still more desirable range is below 4 volume %, and the most desirable range is below 3 volume %.

[0109] Moreover, especially desirable things are vinylene carbonate (VC) and vinyl ethylene carbonate (VEC) among the solvents used as the 4th component.

[0110] Subsequently, a non-aqueous solvent B is explained.

[0111] The reason for specifying the rate to the whole non-aqueous solvent of each solvent in said range is explained.

[0112] a. Gamma-butyrolactone (BL)

Making it 30 - 85 volume % depends the rate of an abundance ratio of BL in a non-aqueous solvent (z) on the same reason as the non-aqueous solvent A mentioned above explained. The more desirable range is below 85 volume % more than 35 volume %, the still more desirable range is below 75 volume % more than 35 volume %, and the most desirable ratio is below 75 volume % more than 55 volume %.

[0113] b. Ethylene carbonate (EC)

Making it 15 - 50 volume % depends the rate of an abundance ratio of EC in a non-aqueous solvent (x) on the same reason as the non-aqueous solvent A mentioned above explained. The more desirable range is below 50 volume % more than 20 volume %, and the still more desirable range is below 40 volume % more than 20 volume %.

[0114] c. Propylene carbonate (PC)

Making it 2 - 35 volume % depends the rate of an abundance ratio of PC in a non-aqueous solvent (y) on the same reason as the non-aqueous solvent A mentioned above explained. The more desirable range is below 30 volume % more than 2 volume %, the more desirable range is below 25 volume % more than 2 volume %, and the still more desirable range is below 20 volume % more than 2 volume %. The most desirable range is below 20 volume % more than 3 volume %.

[0115]

d. If the ratio (w) to the whole non-aqueous solvent of vinylene carbonate (VC) VC is made under into 0.05 volume %, it may be hard coming to carry out eburation of the protective coat on the front face of a negative electrode, the reaction of a negative electrode and BL may progress, and it may become difficult to fully improve a charge-and-discharge cycle property and a low-temperature discharge property. On the other hand, if the ratio of VC exceeds 5 volume %, there is a possibility that the generation of gas at the time of elevated-temperature storage and an initial charge may become remarkable, and it may become difficult to fully improve a charge-and-discharge cycle property. The more desirable range of the ratio of VC is below 3 volume % more than 0.1 volume %, and the still more desirable range is below 2 volume % more than 0.2 volume %.

[0116] In addition, VC moves to the front face of said negative electrode from said non-aqueous solvent into an initial-charge-and-discharge process, and adheres to the front face of said negative electrode. Therefore, in the non-aqueous solvent which exists in the rechargeable battery with which the initial-charge-and-discharge process was given, there are few rates of VC to the whole non-aqueous solvent than rechargeable battery assembly before. Percentage reduction becomes 70 - 80%, when the addition of VC is 1 % of the weight (that is, a survival rate 20 - 30%).

[0117] While being able to make higher effectiveness which controls the generation of gas at the time of elevated-temperature storage when said x in said non-aqueous solvent, said y, said z, and said w fill  $20 \leq x \leq 50$ ,  $2 \leq y \leq 25$ ,  $35 \leq z \leq 75$ , and  $0.1 \leq w \leq 3$  especially, respectively, the discharge capacity under the low-temperature environment near -20 degree C can be improved more. Furthermore, as for a desirable non-aqueous solvent, said x, said y, said z, and said w fill  $20 \leq x \leq 40$ ,  $3 \leq y \leq 20$ ,  $55 \leq z \leq 75$ , and  $0.2 \leq w \leq 2$ , respectively.

[0118] Subsequently, a non-aqueous solvent C is explained.

[0119] The reason for specifying the rate to the whole non-aqueous solvent of each solvent in said range is explained.

[0120] a. Gamma-butyrolactone (BL)

Making it 30 - 85 volume % depends the rate of an abundance ratio of BL in a non-aqueous solvent (z) on the same reason as the non-aqueous solvent A mentioned above explained. The more desirable range is below 85 volume % more than 35 volume %, the still more desirable range is below 75 volume % more than 35 volume %, and the most

desirable ratio is below 75 volume % more than 55 volume %.

[0121] b. Ethylene carbonate (EC)

Making it 15 - 50 volume % depends the rate of an abundance ratio of EC in a non-aqueous solvent (x) on the same reason as the non-aqueous solvent A mentioned above explained. The more desirable range is below 50 volume % more than 20 volume %, and the still more desirable range is below 40 volume % more than 20 volume %.

[0122] c. Propylene carbonate (PC)

Making it 2 - 35 volume % depends the rate of an abundance ratio of PC in a non-aqueous solvent (y) on the same reason as the non-aqueous solvent A mentioned above explained. The more desirable range is below 30 volume % more than 2 volume %, the still more desirable range is below 25 volume % more than 2 volume %, and the still more desirable range is below 20 volume % more than 2 volume %. The most desirable range is below 20 volume % more than 3 volume %.

[0123] d. Vinylene carbonate (VC)

If the rate of an abundance ratio of VC in a non-aqueous solvent (w) exceeds 5 volume %, the generation of gas at the time of elevated-temperature storage and an initial charge becomes remarkable, or the coat formed in a negative-electrode front face will become thick, and it will become difficult for the impedance of a negative electrode to increase and to acquire the outstanding charge-and-discharge cycle property and a low-temperature discharge property. Moreover, if the rate of an abundance ratio of VC is made under into 0.05 volume %, since it cannot become difficult for whenever [ precise ], and thickness of the protective coat formed in a negative-electrode front face to be insufficient, and to fully improve a charge-and-discharge cycle property and a low-temperature discharge property or it may become impossible to control the self-discharge at the time of elevated-temperature storage, as for the ratio to the whole non-aqueous solvent of VC, it is desirable to carry out within the limits of 0.05 volume % - 5 volume %. The more desirable range of the ratio of VC is below 3 volume % more than 0.1 volume %, and the still more desirable range is below 2 volume % more than 0.2 volume %.

[0124] e. If the ratio (q) to the whole non-aqueous solvent of the 5th component of the 5th component exceeds 5 volume %, the generation of gas at the time of elevated-temperature storage and an initial charge becomes remarkable, or the coat formed in a negative-electrode front face will become thick, and it will become difficult for the impedance of a negative electrode to increase and to acquire the outstanding charge-and-discharge cycle property and a low-temperature discharge property. Moreover, if the ratio to the whole non-aqueous solvent of the 5th component is made under into 0.05 volume % It becomes difficult for whenever [ precise ], and thickness of the protective coat formed in a negative-electrode front face to be insufficient, and to fully improve a charge-and-discharge cycle property and a low-temperature discharge property, or Or since it may become impossible to control the self-discharge at the time of elevated-temperature storage, as for the ratio to the whole non-aqueous solvent of the 5th component, it is desirable to carry out within the limits of 0.05 volume % - 5 volume %. Moreover, as for the rate of a sum total abundance ratio of VC and the 5th component to the whole non-aqueous solvent, it is desirable to hold down to below 5 volume %.

[0125] When using vinyl ethylene carbonate (VEC) as the 5th component, the desirable range is 0.05 volume % - 5 volume %, the still more desirable range is 0.1 volume % - 4

volume %, and the most desirable range is 0.2 volume % - 3 volume %.

[0126] When using an ethylene ape fight (ES) as the 5th component, the desirable range is below 5 volume %, the still more desirable range is below 3 volume %, and the most desirable range is below 1.5 volume %.

[0127] When using phenylethylene carbonate (phEC) as the 5th component, the desirable range is below 5 volume %, the still more desirable range is below 4 volume %, and the most desirable range is below 3 volume %.

[0128] When using 12-crown -4 as the 5th component, the desirable range is below 5 volume %, the still more desirable range is below 4 volume %, and the most desirable range is below 3 volume %.

[0129] When using tetraethylene glycol wood ether as the 5th component, the desirable range is below 5 volume %, the still more desirable range is below 4 volume %, and the most desirable range is below 3 volume %.

[0130] Moreover, especially a desirable thing is vinyl ethylene carbonate (VEC) among the solvents used as the 5th component.

[0131] As lithium salt dissolved in this non-aqueous-solvent A-C, it is lithium perchlorate ( $\text{LiClO}_4$ ), 6 phosphorus-fluoride acid lithium ( $\text{LiPF}_6$ ), hoe lithium fluoride ( $\text{LiBF}_4$ ), 6 fluoride arsenic lithium ( $\text{LiAsF}_6$ ), trifluoro meta-sulfonic-acid lithium ( $\text{LiCF}_3\text{SO}_3$ ), and bis-trifluoromethylsulfonyl imide lithium [ $(\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ] etc. can be mentioned.), for example. It is  $\text{LiPF}_6$  especially. Or  $\text{LiBF}_4$  Using is desirable. the most desirable lithium salt --  $\text{LiBF}_4$  it is .

[0132] As for the amount of dissolutions to said non-aqueous solvent of said lithium salt, it is desirable to be referred to as 0.5-2.5mol/L. Still more desirable range is 1-2.5mol/L.

[0133] It is desirable to make said liquefied nonaqueous electrolyte contain a surfactant like trioctylphosphate (TOP), in order to improve wettability with a separator. 3% or less of the addition of a surfactant is desirable, and it is desirable to make it further 0.1 - 1% of within the limits.

[0134] As for the amount of said liquefied nonaqueous electrolyte, it is desirable to make it per [ 0.3-0.7g ] cell unit capacity 100mAh. The more desirable range of the amount of liquefied nonaqueous electrolyte is 0.35-0.55g/100mAh.

[0135] 6) Sheathing material (stowage container)

The configuration of a sheathing material can be made for example, a closed-end cylindrical shape, closed-end rectangle telescopic, saccate, etc.

[0136] This sheathing material can be formed from the sheet containing for example, a resin layer, a metal plate, a metal film, etc.

[0137] The resin layer contained in said sheet can be formed from polyethylene, polypropylene, etc. It is desirable to use the sheet with which the metal layer and the protective layer arranged to both sides of said metal layer were unified as said sheet. Said metal layer makes the role which intercepts moisture. Said metal layer can mention aluminum, stainless steel, iron, copper, nickel, etc. Aluminum with the function it is lightweight and high especially, which intercepts moisture is desirable. Although said metal layer may be formed from one kind of metal, it may be formed from the thing which made two or more kinds of metal layers unify. The protective layer which touches the exterior between said two protective layers makes the role which prevents damage on said metal layer. This external protective layer is formed from one kind of resin layer, or two or more kinds of resin layers. On the other hand, an internal protective layer bears the

role which prevents that said metal layer is corroded by nonaqueous electrolyte. This internal protective layer is formed from one kind of resin layer, or two or more kinds of resin layers. Moreover, thermoplastics can be arranged on the front face of this internal protective layer.

[0138] Said metal plate and said metal film can be formed from iron, stainless steel, and aluminum.

[0139] Thickness (thickness of the wall of a sheathing material) of a sheathing material is set to 0.3mm or less. This is based on the following reasons. If thickness is thicker than 0.3mm, it will become that it can be hard to obtain high weight energy density and volume energy density. The range where the thickness of a sheathing material is desirable is 0.25mm or less, the still more desirable range is 0.15mm or less, and the most desirable range is 0.12mm or less. Moreover, when thickness is thinner than 0.05mm, as for deformation or the lower limit of the thickness of a sheathing material since it becomes easy to damage, it is desirable to make it 0.05mm.

[0140] The thickness of a sheathing material is measured by the approach explained below. That is, in the field except the closure section of a sheathing material, mutually, it separates 1cm or more, and three existing points are chosen as arbitration, the thickness of each point is measured, and the average is computed, and let this value be the thickness of a sheathing material. In addition, when the foreign matter (for example, resin) has adhered to the front face of said sheathing material, thickness is measured after removing this foreign matter. For example, measurement of thickness is performed after removing PVdF by wiping off the front face of said sheathing material with a dimethylformamide solution, when PVdF has adhered to the front face of said sheathing material.

[0141] It is desirable to form a glue line in a part of front face [ at least ] of said sheathing material, and to paste up said electrode group on the inside of said sheathing material by said glue line. If it is made such a configuration, since said sheathing material is fixable to the front face of said electrode group, it can suppress that the electrolytic solution permeates between an electrode group and a sheathing material.

[0142] To said rechargeable battery, it is desirable under 15 degrees C - 80 degrees C temperature conditions to perform an initial charge at the rate of 0.05 or more C and 0.8 C or less. Charge on this condition is good only 1 cycle, and good in a line more than a two cycle. Moreover, you may keep it under a 15 degrees C - 80 degrees C temperature condition before an initial charge for 1 hour to about 20 hours.

[0143] Here, 1C is a current value required in order to discharge nominal capacity (Ah) in 1 hour.

[0144] Specifying the temperature of said initial charge in said range is based on the following reasons. Since the viscosity of liquefied nonaqueous electrolyte is still high in initial charge temperature being less than 15 degrees C, it becomes difficult to infiltrate liquefied nonaqueous electrolyte into homogeneity to a positive electrode, a negative electrode, and a separator, internal impedance increases, and the utilization factor of an active material falls. On the other hand, if initial charge temperature exceeds 80 degrees C, the binder contained in a positive electrode and a negative electrode will deteriorate. The range of desirable charge temperature is 15-60 degrees C, and the still more desirable range is 20-50 degrees C.

[0145] Since expansion of the positive electrode by charge and a negative electrode can



be moderately made late by making the rate of an initial charge into the range of 0.05-0.8C, liquefied nonaqueous electrolyte can be made to permeate a positive electrode and a negative electrode at homogeneity. The rates of a desirable initial charge are 0.05-0.5C. [0146] Since liquefied nonaqueous electrolyte can be infiltrated into the opening of an electrode or a separator by providing such a process at homogeneity, internal impedance of a rechargeable battery can be made small. Consequently, since the utilization factor of an active material can be increased, capacity of a substantial cell can be enlarged. Moreover, the charge-and-discharge cycle property and high current discharge property of a cell can be raised.

[0147] The thin rechargeable lithium-ion battery which is an example of the nonaqueous electrolyte rechargeable battery (I) concerning this invention is explained to a detail with reference to drawing 1 and drawing 2 .

[0148] The sectional view showing the thin rechargeable lithium-ion battery whose drawing 1 is an example of the nonaqueous electrolyte rechargeable battery (I) concerning this invention, and drawing 2 are the expanded sectional views showing the A section of drawing 1 .

[0149] As shown in drawing 1 , the electrode group 2 is contained in the sheathing material 1 whose thickness X is 0.3mm or less. Said electrode group 2 has the structure where the laminated material which consists of a positive electrode, a separator, and a negative electrode was wound around the flat configuration. As said laminated material is shown in drawing 2 (from the drawing bottom) A separator 3, the positive-electrode layer 4 and the positive-electrode charge collector 5, the positive electrode 6 equipped with the positive-electrode layer 4, a separator 3 and the negative-electrode layer 7, the negative-electrode charge collector 8, the negative electrode 9 equipped with the negative-electrode layer 7, a separator 3 and the positive-electrode layer 4, the positive-electrode charge collector 5, the positive electrode 6 equipped with the positive-electrode layer 4, a separator 3 and the negative-electrode layer 7, and the negative-electrode charge collector 8 The negative electrode 9 which it had carried out the laminating to this sequence. As for said electrode group 2, said negative-electrode charge collector 8 is located in the outermost layer. The end was connected to said positive-electrode charge collector 5 of said electrode group 2, and, as for the band-like positive-electrode lead 10, the other end has extended from said sheathing material 1. On the other hand, the end was connected to said negative-electrode charge collector 8 of said electrode group 2, and, as for the band-like negative-electrode lead 11, the other end has extended from said sheathing material 1.

[0150] Subsequently, the nonaqueous electrolyte rechargeable battery (II) concerning this invention is explained.

[0151] This nonaqueous electrolyte rechargeable battery possesses the electrode group by which thickness is contained in a sheathing material 0.3mm or less and said sheathing material. Said electrode group is arranged [ lithium ion ] in occlusion, the positive electrode to emit, and a lithium ion between occlusion, the negative electrode to emit, and said positive electrode and said negative electrode, and contains the electrolyte layer containing a polymer with the function to make nonaqueous electrolyte and this nonaqueous electrolyte gel.

[0152] Having explained in the nonaqueous electrolyte rechargeable battery (I) mentioned above and the same thing are used for a sheathing material, a positive electrode, a negative electrode, and nonaqueous electrolyte.

[0153] Said electrolyte layer is produced by the approach explained below. First, it is made to dry after forming the paste prepared by mixing a polymer and nonaqueous electrolyte with the function to make nonaqueous electrolyte gel. The obtained thin film is made to intervene between a positive electrode and a negative electrode, and an electrode group is produced. After infiltrating nonaqueous electrolyte into this electrode group, said electrolyte layer is obtained by making said thin film plasticize under reduced pressure.

[0154] As for said polymer, it is desirable to have thermoplasticity. As this polymer, at least one kind chosen from polyvinylidene fluoride (PVdF), a polyacrylonitrile (PAN), polyethylene oxide (PEO), a polyvinyl chloride (PVC), polyacrylate (PMMA), and polyvinylidene fluoride hexafluoropropylene (PVdF-HFP) can be used, for example.

[0155] To said rechargeable battery, it is desirable under 15 degrees C - 80 degrees C temperature conditions to perform an initial charge at the rate of 0.05 or more C and 0.8 C or less. Charge on this condition is good only 1 cycle, and good in a line more than a two cycle. Moreover, you may keep it under a 15 degrees C - 80 degrees C temperature condition before an initial charge for 1 hour to about 20 hours.

[0156] Thickness is held at a sheathing material 0.3mm or less, the electrode group contained in said sheathing material, and said electrode group, and, as for the nonaqueous electrolyte rechargeable battery concerning this invention explained above, possesses the nonaqueous electrolyte containing the lithium salt dissolved in a non-aqueous solvent and said non-aqueous solvent. Said non-aqueous solvent Ethylene carbonate (EC), propylene carbonate (PC), Gamma-butyrolactone (BL) and vinylene carbonate (VC) are included. Ethylene carbonate, propylene carbonate to said whole non-aqueous solvent, When the rate of gamma-butyrolactone and vinylene carbonate is set to x (volume %), and y (volume %), z (volume %) and w (volume %), respectively, said x, said y, said z, and said w fill  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0.05 \leq w \leq 5$ , respectively.

[0157] In order to improve the weight energy density and volume energy density of a nonaqueous electrolyte rechargeable battery, it is indispensable to set thickness of a sheathing material to 0.3mm or less. However, it has the trouble of being easy to swell by the gas by which thickness generated the sheathing material 0.3mm or less in the sheathing material.

[0158] Positive active material and nonaqueous electrolyte can control that nonaqueous electrolyte carries out oxidative degradation in response to the storage under a high temperature service, and the time of an initial charge by making the rate of gamma-butyrolactone to said whole non-aqueous solvent below into 85 volume % more than 30 volume %. Consequently, since the amount of generation of gas can be lessened, it can stop that a sheathing material blisters.

[0159] Moreover, a precise protective coat can be formed on the surface of a negative electrode by making the rate of ethylene carbonate to said whole non-aqueous solvent below into 50 volume % more than 15 volume %, and making the rate of propylene carbonate below into 35 volume % more than 2 volume %, and making the rate of vinylene carbonate below into 5 volume % more than 0.05 volume %. Consequently, since it can control that a negative electrode and gamma-butyrolactone react and reduction decomposition of nonaqueous electrolyte arises, the rise of the interface impedance of a negative electrode can be controlled and a charge-and-discharge cycle life and a low-temperature discharge property can be improved. If only either PC or the VC

are added to the non-aqueous solvent which consists of EC and BL, it becomes difficult to become what has the inadequate compactness of the protective coat formed in a negative-electrode front face, and to fully control the reaction of a negative electrode and gamma-butyrolactone. Therefore, the rechargeable battery equipped with the nonaqueous electrolyte containing the non-aqueous solvent which consists of either PC or the VC, and EC and BL cannot obtain a longevity life.

[0160] As explained above, according to this invention, the nonaqueous electrolyte rechargeable battery which can aim at improvement in weight energy density and volume energy density, and the generation of gas at the time of elevated-temperature storage and an initial charge is controlled, and is excellent in a charge-and-discharge cycle life and a low-temperature discharge property is realizable.

[0161] Thickness is contained in a sheathing material 0.3mm or less and said sheathing material, and, as for the nonaqueous electrolyte rechargeable battery concerning this invention, possesses the separator arranged in a lithium ion between occlusion, the positive electrode to emit and a negative electrode, and said positive electrode in said sheathing material and said negative electrode, and the liquefied nonaqueous electrolyte containing the lithium salt which it sinks into said separator at least, and is dissolved in a non-aqueous solvent and said non-aqueous solvent. When said non-aqueous solvent sets the rate of the ethylene carbonate and propylene carbonate to said whole non-aqueous solvent, gamma-butyrolactone, and vinylene carbonate to x (volume %), and y (volume %), z (volume %) and w (volume %) including ethylene carbonate, propylene carbonate, gamma-butyrolactone, and vinylene carbonate, respectively, said x, said y, said z, and said w fill  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0.05 \leq w \leq 5$ , respectively.

[0162] According to such a rechargeable battery, since liquefied nonaqueous electrolyte is used, ionic conductivity can be made high and interfacial resistance of a negative electrode and a separator can be made small at the interfacial resistance list of a positive electrode and a separator. Consequently, since a charge-and-discharge cycle life and a low-temperature discharge property can be raised further, the nonaqueous electrolyte rechargeable battery with which it was possible to have aimed at improvement in weight energy density and volume energy density with the rechargeable battery, and the generation of gas at the time of elevated-temperature storage and an initial charge was controlled, and the charge-and-discharge cycle life and the low-temperature discharge property have been improved by leaps and bounds is realizable.

[0163] Thickness another nonaqueous electrolyte rechargeable battery concerning this invention A sheathing material 0.3mm or less, In the nonaqueous electrolyte rechargeable battery possessing the electrode group contained in said sheathing material, and the nonaqueous electrolyte containing the lithium salt which is held at said electrode group and dissolved in a non-aqueous solvent A and said non-aqueous solvent A Said non-aqueous solvent A Ethylene carbonate and propylene carbonate, Gamma-butyrolactone, and vinylene carbonate, vinyl ethylene carbonate, The 4th component which consists of one or more kinds of solvents chosen from the group which consists of an ethylene ape fight, phenylethylene carbonate, 12-crown -4, and tetraethylene glycol wood ether is included. Ethylene carbonate, propylene carbonate to said whole non-aqueous-solvent A, The rate of gamma-butyrolactone and said 4th component, respectively x (volume %), When referred to as y (volume %), z (volume %), and p (volume %), said x, said y, said z,

and said p are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0 < p \leq 5$ , respectively.

[0164] Although the nonaqueous electrolyte containing gamma-butyrolactone has the effectiveness of suppressing an initial charge and the generation of gas at the time of elevated-temperature storage, it causes decline in the capacity recovery factor at the time of self-discharge becoming easy to progress and carrying out a recharge after storage at the time of elevated-temperature storage. According to the rechargeable battery concerning this invention, it becomes possible to suppress advance of the self-discharge at the time of elevated-temperature storage, and to improve a charge-and-discharge cycle property, controlling an initial charge and the generation of gas at the time of elevated-temperature storage.

[0165] Especially x in a non-aqueous solvent A, and y, z and p, respectively  $20 \leq x \leq 50$ ,  $2 \leq y \leq 25$ ,  $35 \leq z \leq 75$ ,  $0 < p \leq 4$ , and by making it still more desirably  $20 \leq x \leq 40$ ,  $2 \leq y \leq 20$ ,  $55 \leq z \leq 75$ , and  $0 < p \leq 3$  The both sides of a self-discharge property and a charge-and-discharge cycle property are more improvable, controlling the generation of gas at the time of an initial charge and elevated-temperature storage.

[0166] Another nonaqueous electrolyte rechargeable battery to the pan concerning this invention In the nonaqueous electrolyte rechargeable battery possessing the nonaqueous electrolyte in which thickness contains the lithium salt which it is held at a sheathing material 0.3mm or less, the electrode group contained in said sheathing material, and said electrode group, and dissolves in a non-aqueous solvent C and said non-aqueous solvent C Said non-aqueous solvent C Ethylene carbonate and propylene carbonate, Gamma-butyrolactone, vinylene carbonate, and vinyl ethylene carbonate, The 5th component which consists of one or more kinds of solvents chosen from the group which consists of an ethylene ape fight, phenylethylene carbonate, 12-crown -4, and tetraethylene glycol wood ether is included. Ethylene carbonate, propylene carbonate to said whole non-aqueous-solvent C, The rate of gamma-butyrolactone, vinylene carbonate, and said 5th component, respectively x (volume %), When referred to as y (volume %), z (volume %), w (volume %), and q (volume %), said x, said y, said z, said w, and said q are characterized by filling  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ ,  $0 < w \leq 5$ , and  $0 < q \leq 5$ , respectively.

[0167] According to such a rechargeable battery, it becomes possible to suppress advance of the self-discharge at the time of elevated-temperature storage, and to improve a charge-and-discharge cycle property, controlling an initial charge and the generation of gas at the time of elevated-temperature storage.

[0168] Especially x in a non-aqueous solvent C, and y, z, w and q, respectively  $20 \leq x \leq 50$ ,  $2 \leq y \leq 25$ ,  $35 \leq z \leq 75$ ,  $0 < w \leq 3$ ,  $0 < q \leq 4$ , and by making it still more desirably  $20 \leq x \leq 40$ ,  $2 \leq y \leq 20$ ,  $55 \leq z \leq 75$ ,  $0 < w \leq 2$ , and  $0 < q \leq 3$  The both sides of a self-discharge property and a charge-and-discharge cycle property are more improvable, controlling the generation of gas at the time of an initial charge and elevated-temperature storage.

[0169]

[Example] Hereafter, it explains to a detail with reference to the drawing which mentioned the example of this invention above.

[0170] (Example 1)

<production of a positive electrode> -- first, 91 % of the weight of lithium cobalt oxide

( $\text{Li}_x\text{CoO}_2$ , however  $x$  are  $0 < x \leq 1$ ) powder was added as 3 % of the weight of acetylene black, 3 % of the weight of graphite, and a binder, the N-methyl-2-pyrrolidone (NMP) was added as 3 % of the weight (PVdF) of polyvinylidene fluorides, and a solvent, it mixed, and the slurry was prepared. Electrode consistencies are 3 g/cm<sup>3</sup> by drying and pressing, after applying said slurry to both sides of the charge collector with which thickness consists of aluminium foil which is 15 micrometers. The positive electrode of the structure where the positive-electrode layer was supported by both sides of a charge collector was produced.

[0171] 7 % of the weight (PVdF) of polyvinylidene fluorides was mixed with 93 % of the weight for the powder of a mesophase pitch based carbon fiber (for 8 micrometers and mean fiber length, 20 micrometers and an average spacing (d002) are [ the diameter of fiber ] 0.3360nm) heat-treated at 3000 degrees C as a <production of negative electrode> carbonaceous ingredient as a binder, and the slurry was prepared. Electrode consistencies are 1.4 g/cm<sup>3</sup> by applying said slurry to both sides of the charge collector with which thickness consists of copper foil which is 12 micrometers, and drying and pressing it in them. The negative electrode of the structure where the negative-electrode layer was supported by the charge collector was produced.

[0172] 25 micrometers, 120 degrees C, and a heat shrink in 1 hour prepared [ <separator> thickness ] the separator which consists of a porosity film made from polyethylene whose porosity is 50% at 20%.

[0173] <Preparation of nonaqueous electrolyte> ethylene carbonate (EC), propylene carbonate (PC), gamma-butyrolactone (BL), and vinylene carbonate (VC) were mixed so that the rate (EC:PC:BL:VC) of a volume ratio might be set to 25:2:72:1, and the non-aqueous solvent was prepared. 4 lithium borate fluoride ( $\text{LiBF}_4$ ) was dissolved in the obtained non-aqueous solvent so that the concentration might be set to 1.5 mols / L, and nonaqueous electrolyte was prepared.

[0174] After welding the band-like positive-electrode lead to the charge collector of the <production of electrode group> aforementioned positive electrode, welding a band-like negative-electrode lead to the charge collector of said negative electrode and winding said positive electrode and said negative electrode around a curled form through said separator between them, it fabricated in the shape of flat, and the electrode group was produced.

[0175] Press forming was performed for 25 seconds by the pressure of 13kg/cm<sup>2</sup>, heating this electrode group at 90 degrees C, and said positive electrode, said negative electrode, and said separator were made to unify.

[0176] The laminate film with a thickness of 100 micrometers which covered both sides of aluminium foil with polypropylene was fabricated to saccate, and said electrode group was contained to this.

[0177] Subsequently, the moisture contained in said electrode group and said laminate film was removed by performing a vacuum drying to the electrode group in said laminate film at 80 degrees C for 12 hours.

[0178] It pours into the electrode group in said laminate film so that the amount per cell capacity 1Ah may be set to 4.8g in said nonaqueous electrolyte, and it has drawing 1 mentioned above and the structure shown in 2, and thickness assembled the thin nonaqueous electrolyte rechargeable battery 35mm and whose height 3.6mm and width of face are 62mm.

[0179] The following measures were taken as an initial-charge-and-discharge process to this nonaqueous electrolyte rechargeable battery. First, after leaving 2h under 45-degree C hot environments, constant current and constant-potential charge were performed to 4.2V by 0.2C (104mA) under the environment for 15 hours. Then, it was left at 20 degrees C for seven days. It discharged to 3.0V by 0.2C under the 20 more-degree C environment, and the nonaqueous electrolyte rechargeable battery was manufactured.

[0180] (Examples 2-22) Except changing the presentation of a non-aqueous solvent, as shown in the following table 1, the thin nonaqueous electrolyte rechargeable battery was manufactured like the example 1 mentioned above.

[0181] (Examples 1-11 of a comparison) Except changing a presentation and lithium salt of a non-aqueous solvent, as shown in the following table 2, the thin nonaqueous electrolyte rechargeable battery was manufactured like the example 1 mentioned above.

[0182] About the rechargeable battery of the acquired examples 1-22 and the examples 1-11 of a comparison, the cell property was evaluated by the approach explained below.

[0183] 1) The cycle of 3-hour charge of the 4.2V constant current and the constant voltage in 1C rate and 3.0V discharge of 1C rate was repeated under the environment of 20 degrees C of capacity maintenance factors after the 400 cycles under 20 degree-C environment, and the capacity maintenance factor after 400 cycles and the maximum discharge capacity in 400 cycles were measured. The result is written together to the following tables 1 and 2.

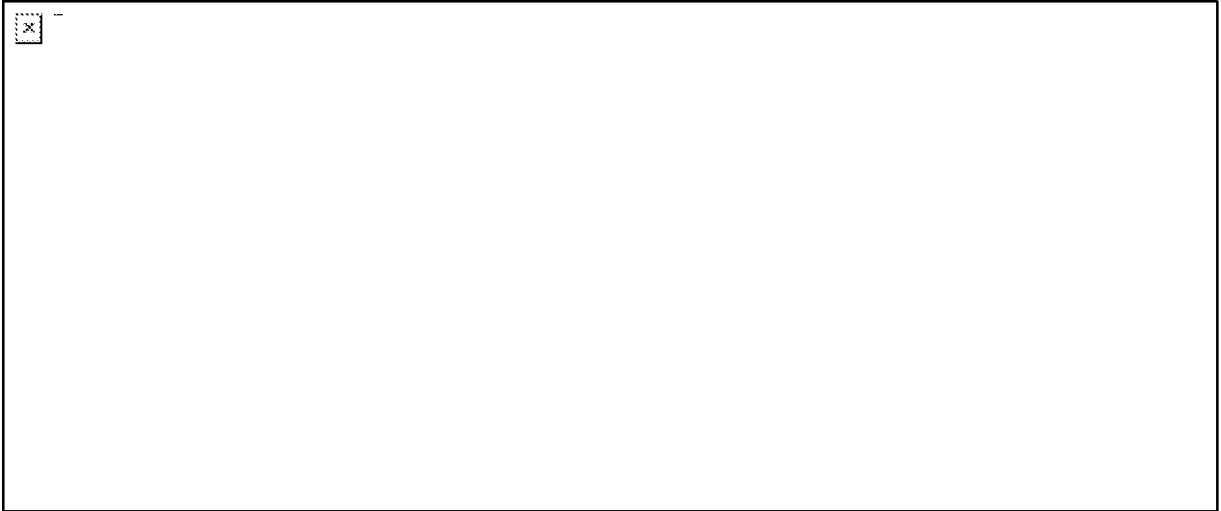
[0184] 2) Repeat the cycle of 3-hour charge of the 4.2V constant current and the constant voltage in the current of 1C, and 3.0V discharge with the current of 1C under the environment of 45 degrees C of capacity maintenance factors after the 200 cycles under 45 degree-C environment, measure the capacity maintenance factor after 200 cycles, and write together the result to the following tables 1 and 2.

[0185] 3) In order to investigate the self-discharge property under the self-discharge property hot environments under 65 degree-C environment, Under a 20-degree C environment, after 10-hour charge of the 4.2V constant current and the constant voltage in the current of 0.2C, and 10-hour discharge of the 3.4V constant current and the constant voltage in the current of 0.2C, It is left in a 65-degree C thermostat, and acts as the monitor of the cell voltage, the time amount taken for cell voltage to amount to 2.5V by self-discharge is measured, and the result is written together to the following tables 1 and 2.

[0186] 4) In order to investigate cell bulging by storage in the bottom of the bulging hot environments at the time of storing in the bottom of 85 degree-C environment, and the charge condition, the cell was left in the 85-degree C thermostat under the 20-degree C environment for 120 hours after 3-hour charge of the 4.2V constant current and the constant voltage in the current of 1C. Then, a cell is picked out from a thermostat, after leaving a cell under a 20-degree C environment for 2 hours, bulging is measured, and the result is written together to the following tables 1 and 2.

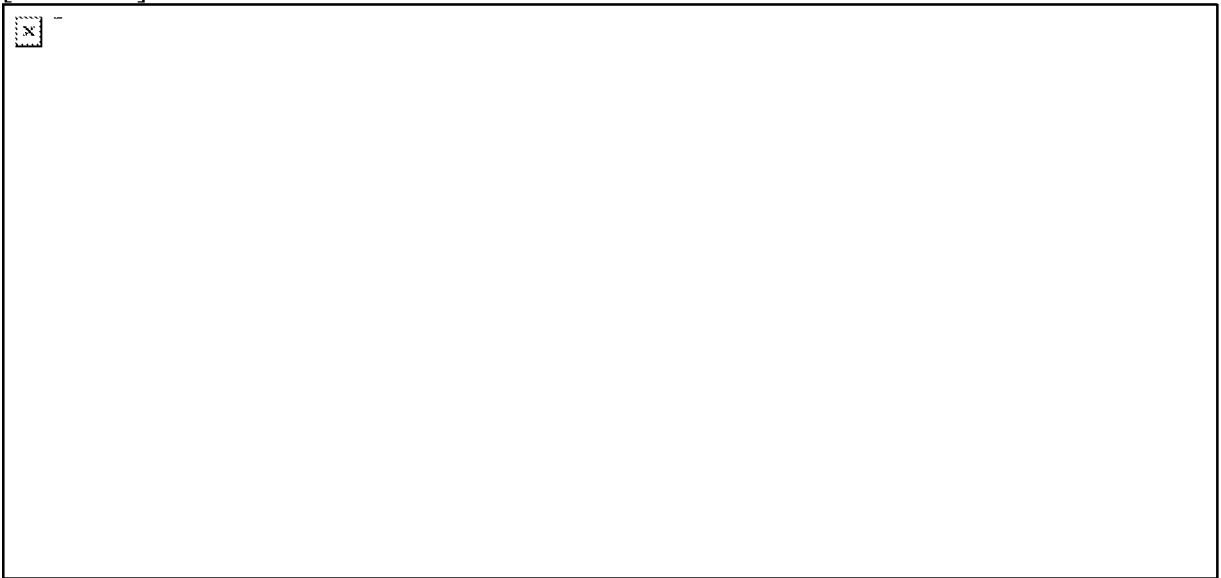
[0187]

[Table 1-1]



[0188]

[Table 1-2]



[0189]

[Table 2]



[0190] A high discharge capacity is obtained, the capacity maintenance factor in an elevated temperature is high in a room temperature list, and the self-discharge under hot environments is suppressed, and the rechargeable battery of the examples 1-22 equipped with the liquefied nonaqueous electrolyte in which the rate of EC, PC, BL, and VC contains the non-aqueous solvent which fills  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0.05 \leq w \leq 5$  so that clearly from Table 1 and 2 is understood that bulging at the time of elevated-temperature storage is small. Especially as for examples 2-7 and the rechargeable battery of 11, 15-18, it turns out that the capacity maintenance factor after 400 cycles is 80% or more.

[0191] On the other hand, as for the rechargeable battery of the examples 1-11 of a comparison, it turns out that the capacity maintenance factor in an elevated temperature all becomes low at a room temperature list compared with examples 1-22.

[0192] Moreover, about the rechargeable battery of an example 1, after said initial-charge-and-discharge process, after opening the circuit wide for 5 hours or more and making potential fully settle down, Ar concentration decomposed at 99.9% or more, the dew-point decomposed in the glove compartment -50 degrees C or less, and the electrode group was taken out. They are a click and dimethyl sulfoxide (DMSO) to a centrifugation tube about said electrode group. - d6 was added and sealed, it took out from said glove compartment, and centrifugal separation was performed. Then, said electrolytic solution and mixed solution of said DMSO-d6 were extracted from said centrifugation tube in said glove compartment. About 0.5ml of said mixed solvents was put into sample tubing for NMR of 5mmphi, and NMR measurement was performed. the equipment used for said NMR measurement -- the JEOL Co., Ltd. make -- it is JNM-LA400WB and, in the observation nucleus,  $^1\text{H}$  and an observation frequency used the internal standard of dimethyl sulfoxide (DMSO)-d5 (2.5 ppm) for 400MHz and a reference material. Measurement temperature was made into 25 degrees C. By  $^1\text{H}$ NMR spectrum, it has checked that VC was contained in the non-aqueous solvent to which the peak near 4.5 ppm and corresponding to VC in the peak corresponding to EC is observed near 7.7 ppm, and exists in the rechargeable battery of the example 1 after an initial-charge-and-



discharge process. Moreover, when asked for the ratio of the NMR integrated intensity of said VC from the NMR integrated intensity of said EC, it turned out that the rate of VC to the whole non-aqueous solvent is decreasing from rechargeable battery assembly before.

[0193] (Example 23)

<Preparation of nonaqueous electrolyte> ethylene carbonate (EC), propylene carbonate (PC), gamma-butyrolactone (BL), and vinylene carbonate (VC) were mixed so that the rate (EC:PC:BL:VC) of a volume ratio might be set to 25:9:65:1, and the non-aqueous solvent was prepared. 4 lithium borate fluoride (LiBF<sub>4</sub>) was dissolved in the obtained non-aqueous solvent so that the concentration might be set to 1.5 mols / L, and nonaqueous electrolyte was prepared.

[0194] As the example 1 of which the <production of electrode group> above-mentioned was done explained, the flat-like electrode group was produced. Hot press was performed on the same conditions, and said positive electrode, said negative electrode, and said separator were made to unify as the example 1 mentioned above in this electrode group explained.

[0195] Thickness fabricated the aluminium sheet whose thickness is 300 micrometers with the can of the rectangular parallelepiped 34mm and whose height are 58mm, and 4mm and width of face contained said electrode group to this.

[0196] Subsequently, the moisture contained in said electrode group and said laminate film was removed by performing a vacuum drying on the same conditions as the example 1 mentioned above in the electrode group in said aluminium can having explained.

[0197] Said nonaqueous electrolyte was poured into the electrode group in said aluminium can so that the amount per cell capacity 1Ah might be set to 4.8g, and the thin nonaqueous electrolyte rechargeable battery was assembled.

[0198] The initial-charge-and-discharge process was given on the same conditions, and the nonaqueous electrolyte rechargeable battery was manufactured as the example 1 mentioned above explained to this nonaqueous electrolyte rechargeable battery.

[0199] (Examples 24-28) Except changing the presentation of a non-aqueous solvent, as shown in the following table 3, the thin nonaqueous electrolyte rechargeable battery was manufactured like the example 23 mentioned above.

[0200] (Examples 12-17 of a comparison) Except changing a presentation and lithium salt of a non-aqueous solvent, as shown in the following table 3, the thin nonaqueous electrolyte rechargeable battery was manufactured like the example 23 mentioned above.

[0201] About the rechargeable battery of the acquired examples 23-28 and the examples 12-17 of a comparison, on the same conditions, a 45-degree C capacity maintenance factor, the maximum discharge capacity, the storage property under 65-degree-C environment, and 85-degree C bulging are measured in a room temperature list, and the result is written together to the following table 3 as the example 1 mentioned above explained.

[0202]

[Table 3]



[0203] A high discharge capacity is obtained, the capacity maintenance factor under hot environments is high in a room temperature list, and the self-discharge at the time of elevated-temperature storage is suppressed, and the rechargeable battery of the examples 23-28 equipped with the liquefied nonaqueous electrolyte in which the rate of EC, PC, BL, and VC contains the non-aqueous solvent which fills  $15 \leq x \leq 50$ ,  $2 \leq y \leq 30$ ,  $35 \leq z \leq 85$ , and  $0.05 \leq w \leq 5$  so that clearly from Table 3 is understood that bulging at the time of elevated-temperature storage is small.

[0204] On the other hand, as for the rechargeable battery of the examples 12-17 of a comparison, it turns out that the capacity maintenance factor in an elevated temperature all becomes low at a room temperature list compared with examples 23-28.

[0205] (Example 29)

<Preparation of nonaqueous electrolyte> ethylene carbonate (EC), propylene carbonate (PC), gamma-butyrolactone (BL), and vinylene carbonate (VC) were mixed so that the rate (EC:PC:BL:VC) of a volume ratio might be set to 25:9:65:1, and the non-aqueous solvent was prepared. 4 lithium borate fluoride ( $\text{LiBF}_4$ ) was dissolved in the obtained non-aqueous solvent so that the concentration might be set to 1.5 mols / L, and nonaqueous electrolyte was prepared. This nonaqueous electrolyte and the solution which dissolved and obtained poly vinylidene fluoride hexafluoropropylene (PVdF-HEP) in the tetra-hydroxy furan (THF) were mixed, and the paste was prepared. After applying the obtained paste to a substrate, the thin film was obtained by making it dry.

[0206] After welding a band-like negative-electrode lead to the charge collector of the same negative electrode as the band-like positive-electrode lead was welded and the example 1 mentioned above explained it to the charge collector of the same positive electrode as the example 1 of which the <production of electrode group> above-

mentioned was done explained and winding said positive electrode and said negative electrode around a curled form through said thin film between them, it fabricated in the shape of flat, and the electrode group was produced.

[0207] You made it immersed in the nonaqueous electrolyte which mentioned this electrode group above, and the electrode group to which the electrolyte layer intervened between the positive electrode and the negative electrode was obtained by making a thin film plasticize under reduced pressure.

[0208] The laminate film with a thickness of 100 micrometers which covered both sides of aluminium foil with polypropylene was fabricated to saccate, said electrode group was contained to this, and thickness assembled the thin nonaqueous electrolyte rechargeable battery 35mm and whose height 3.6mm and width of face are 62mm.

[0209] The following measures were taken as an initial-charge-and-discharge process to this nonaqueous electrolyte rechargeable battery. First, after leaving 2h under 45-degree C hot environments, constant current and constant-potential charge were performed to 4.2V by 0.2C (84mA) under the environment for 15 hours. Then, it was left at 20 degrees C for seven days. It discharged to 3.0V by 0.2C under the 20 more-degree C environment, and the nonaqueous electrolyte rechargeable battery was manufactured.

[0210] (Examples 30-34) Except changing the presentation of a non-aqueous solvent, as shown in the following table 4, the thin nonaqueous electrolyte rechargeable battery was manufactured like the example 29 mentioned above.

[0211] (Examples 18-24 of a comparison) Except changing a presentation and lithium salt of a non-aqueous solvent, as shown in the following table 4, the thin nonaqueous electrolyte rechargeable battery was manufactured like the example 29 mentioned above.

[0212] About the rechargeable battery of the acquired examples 29-34 and the examples 18-24 of a comparison, the cell property was evaluated by the approach explained below.

[0213] 1) The cycle of 3-hour charge of the 4.2V constant current and the constant voltage in 1C rate and 3.0V discharge of 1C rate was repeated under the environment of 20 degrees C of capacity maintenance factors after the 300 cycles under 20 degree-C environment, and the capacity maintenance factor after 300 cycles and the maximum discharge capacity in 300 cycles were measured. The result is written together to the following table 4.

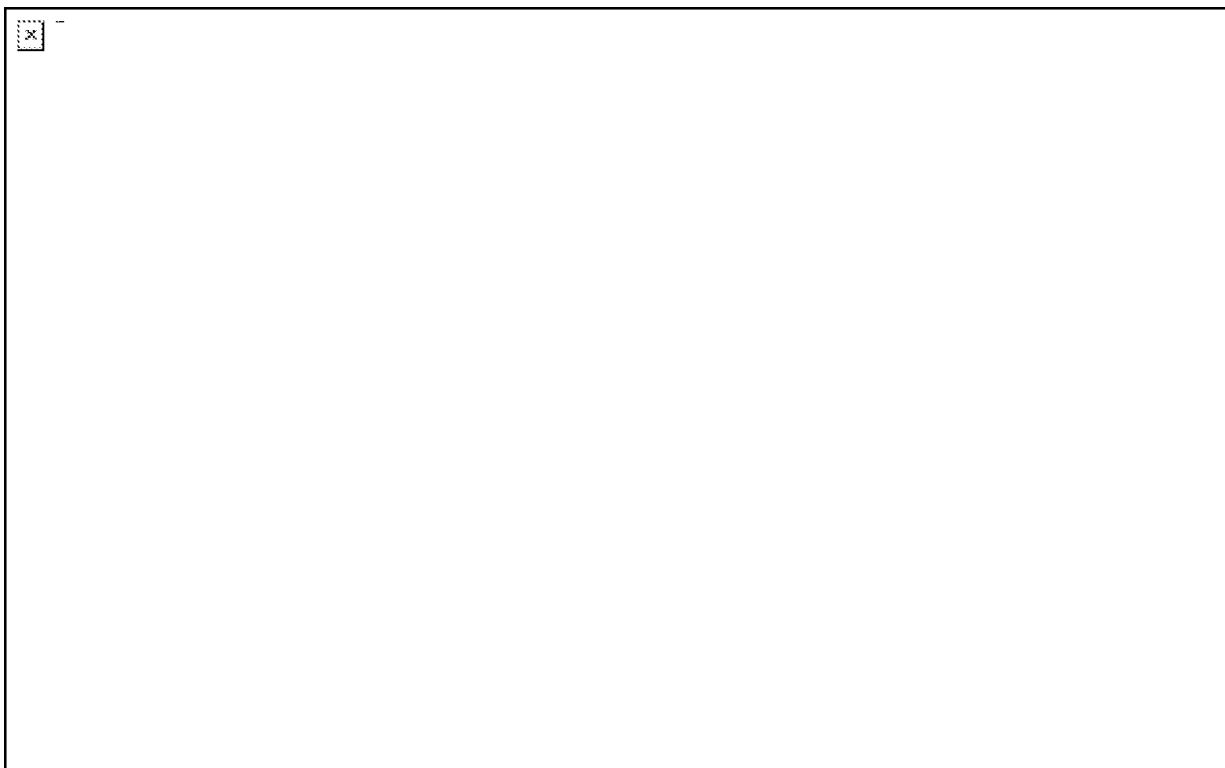
[0214] 2) Repeat the cycle of 3-hour charge of the 4.2V constant current and the constant voltage in the current of 1C, and 3.0V discharge with the current of 1C under the environment of 45 degrees C of capacity maintenance factors after the 200 cycles under 45 degree-C environment, measure the capacity maintenance factor after 200 cycles, and write together the result to the following table 4.

[0215] 3) The same approach estimates the self-discharge property under hot environments, and write together the result to the following table 4 as the example 1 under 65 degree-C environment which carried out the self-discharge property above-mentioned explained.

[0216] 4) The same approach estimates cell bulging by storage in the bottom of hot environments, and the charge condition, and write together the result to the following table 4 as the example 1 which it blistered at the time of storing in the bottom of 85 degree-C environment, and was mentioned above explained.

[0217]

[Table 4]



[0218] The rechargeable battery of the examples 29-34 equipped with the gel nonaqueous electrolyte in which the rate of EC, PC, BL, and VC contains the non-aqueous solvent which fills  $15 \leq x \leq 50$ ,  $2 \leq y \leq 35$ ,  $30 \leq z \leq 85$ , and  $0.05 \leq w \leq 5$  so that clearly from Table 4 It turns out that a high discharge capacity is obtained, the capacity maintenance factor in an elevated temperature is high in a room temperature list, and the self-discharge under hot environments can be controlled, and bulging at the time of elevated-temperature storage can be made small.

[0219] On the other hand, as for the rechargeable battery of the examples 18-24 of a comparison, it turns out that the capacity maintenance factor in an elevated temperature all becomes low at a room temperature list compared with examples 29-34.


[0220] (An example 35 - example 94) Nonaqueous electrolyte was prepared by [ which show the electrolyte of the class shown in following Table 5 - 10 at the non-aqueous solvent which has the presentation shown in following Table 5 - 10 in following Table 5 - 10 ] carrying out the concentration dissolution. Except using this nonaqueous electrolyte, the thin nonaqueous electrolyte rechargeable battery was manufactured like the example 1 mentioned above.

[0221] In addition, in Table 5 - 10, in VEC, phenylethylene carbonate and Crown show 12-crown -4, and, as for vinyl ethylene carbonate and ES, Ether shows tetraethylene glycol wood ether, as for an ethylene ape fight and phEC.

[0222] About the rechargeable battery of the acquired examples 35-94, on the same conditions, a 45-degree C capacity maintenance factor, the maximum discharge capacity, the storage property under 65-degree-C environment, and 85-degree C bulging are measured in a room temperature list, and the result is written together to following Table 5 - 10 as the example 1 mentioned above explained.


[0223]

[Table 5]




[0224]

[Table 6]



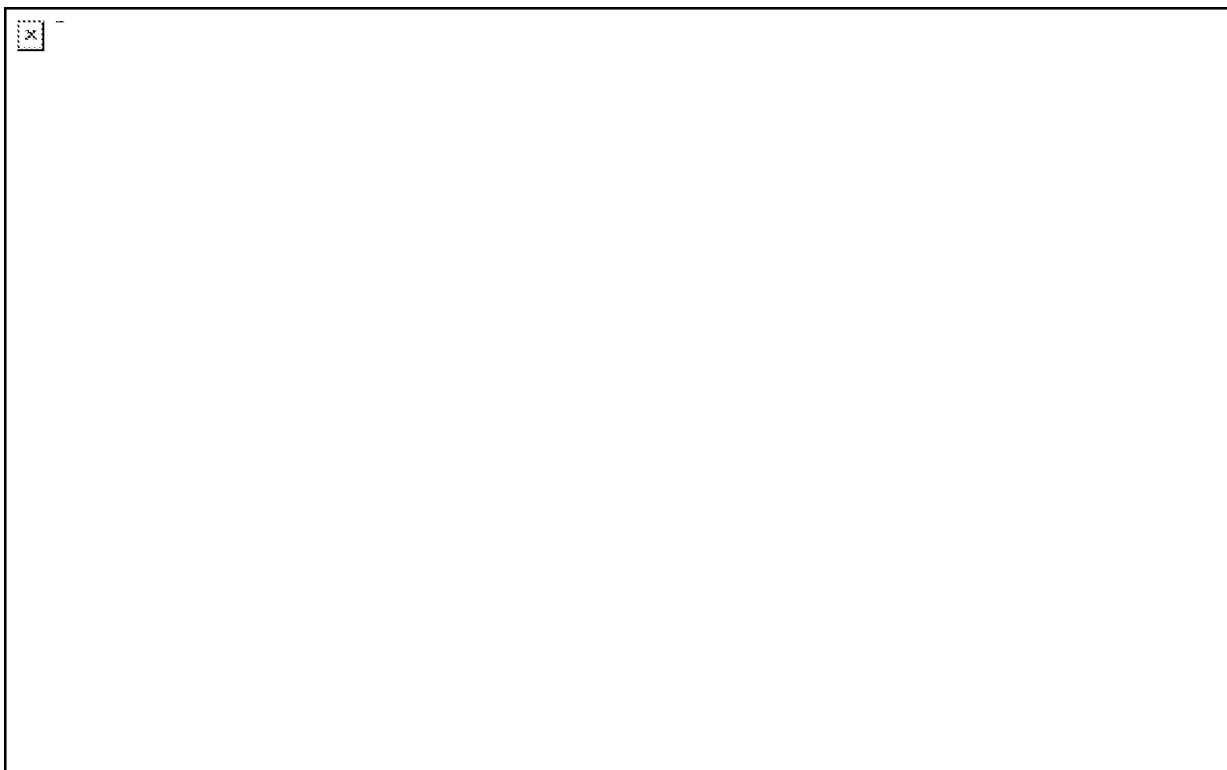
[0225]

[Table 7]



[0226]

[Table 8]




[0227]

[Table 9]



[0228]

[Table 10]


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[0229] By comparing with the examples 1-11 of a comparison of Table 2 which mentioned above the result of above-mentioned Table 5 - 10, a high discharge capacity is obtained, the capacity maintenance factor under hot environments is high in a room temperature list, and the sag by the self-discharge at the time of elevated-temperature storage is controlled, and bulging at the time of elevated-temperature storage is understood that the rechargeable battery of the examples 35-94 equipped with the liquefied nonaqueous electrolyte containing a non-aqueous solvent A or a non-aqueous solvent C is small.

[0230] On the other hand, as for the rechargeable battery of the examples 1-11 of a comparison, it turns out that the capacity maintenance factor in an elevated temperature all becomes low at a room temperature list compared with examples 35-94.

[0231] Moreover, about the rechargeable battery of an example 35, after said initial-charge-and-discharge process, after opening the circuit wide for 5 hours or more and making potential fully settle down, Ar concentration decomposed at 99.9% or more, the dew-point decomposed in the glove compartment -50 degrees C or less, and the electrode group was taken out. They are a click and dimethyl sulfoxide (DMSO) to a centrifugation tube about said electrode group. - d6 was added and sealed, it took out from said glove compartment, and centrifugal separation was performed. Then, said electrolytic solution and mixed solution of said DMSO-d6 were extracted from said centrifugation tube in said glove compartment. About 0.5ml of said mixed solvents was put into sample tubing for NMR of 5mmphi, and NMR measurement was performed. the equipment used for said



NMR measurement -- the JEOL Co., Ltd. make -- it is JNM-LA400WB and, in the observation nucleus,  $^1\text{H}$  and an observation frequency used the internal standard of dimethyl sulfoxide (DMSO)- $d_5$  (2.5 ppm) for 400MHz and a reference material. Measurement temperature was made into 25 degrees C. By  $^1\text{H}$ NMR spectrum, the peak corresponding to EC has checked that VEC was contained in the non-aqueous solvent to which near 4.5 ppm and the peak corresponding to VEC are observed 5.2 and near 5.4 or 6 ppm, and exist in the rechargeable battery of the example 35 after an initial-charge-and-discharge process. Moreover, when asked for the ratio of said NMR integrated intensity of VEC from the NMR integrated intensity of said EC, it turned out that the rate of VEC to the whole non-aqueous solvent is decreasing from rechargeable battery assembly before.  $^1\text{H}$ NMR spectrum of nonaqueous electrolyte used for reference in the example 35 is shown in drawing 3 .

[0232] (Examples 95-104) Nonaqueous electrolyte was prepared by [ which show the electrolyte of the class shown in the following table 11 at the non-aqueous solvent which has the presentation shown in the following table 11 in the following table 11 ] carrying out the concentration dissolution. Except using this nonaqueous electrolyte, the thin nonaqueous electrolyte rechargeable battery was manufactured like the example 23 mentioned above.

[0233] In addition, in Table 11, in VEC, phenylethylene carbonate and Crown show 12-crown -4, and, as for vinyl ethylene carbonate and ES, Ether shows tetraethylene glycol wood ether, as for an ethylene ape fight and phEC.

[0234] About the rechargeable battery of the acquired examples 95-104, on the same conditions, a 45-degree C capacity maintenance factor, the maximum discharge capacity, the storage property under 65-degree-C environment, and 85-degree C bulging are measured in a room temperature list, and the result is written together to the following table 11 as the example 1 mentioned above explained.

[0235]

[Table 11]



[0236] By comparing with the examples 12-17 of a comparison of Table 3 which mentioned above the result of the above-mentioned table 11 shows that a high discharge capacity is obtained, the capacity maintenance factor under hot environments is high in a room temperature list, and the sag by the self-discharge at the time of elevated-temperature storage is controlled, and the rechargeable battery of the examples 95-104 equipped with the liquefied nonaqueous electrolyte containing a non-aqueous solvent A or a non-aqueous solvent C can make small bulging at the time of elevated-temperature storage.

[0237] On the other hand, as for the rechargeable battery of the examples 12-17 of a comparison, it turns out that the capacity maintenance factor in an elevated temperature all becomes low at a room temperature list compared with examples 95-104.

[0238] (Examples 105-124) Nonaqueous electrolyte was prepared by [ which show the electrolyte of the class shown in following Table 12 - 13 at the non-aqueous solvent which has the presentation shown in the following tables 12-13 in following Table 12 - 13 ] carrying out the concentration dissolution. Except using this nonaqueous electrolyte, the thin nonaqueous electrolyte rechargeable battery was manufactured like the example 29 mentioned above.


[0239] In addition, in Table 12 - 13, in VEC, phenylethylene carbonate and Crown show 12-crown -4, and, as for vinyl ethylene carbonate and ES, Ether shows tetraethylene glycol wood ether, as for an ethylene ape fight and phEC.

[0240] About the rechargeable battery of the acquired examples 105-124, on the same conditions, a 45-degree C capacity maintenance factor, the maximum discharge capacity, the storage property under 65-degree-C environment, and 85-degree C bulging are measured in a room temperature list, and the result is written together to following Table

12 - 13 as the example 29 mentioned above explained.

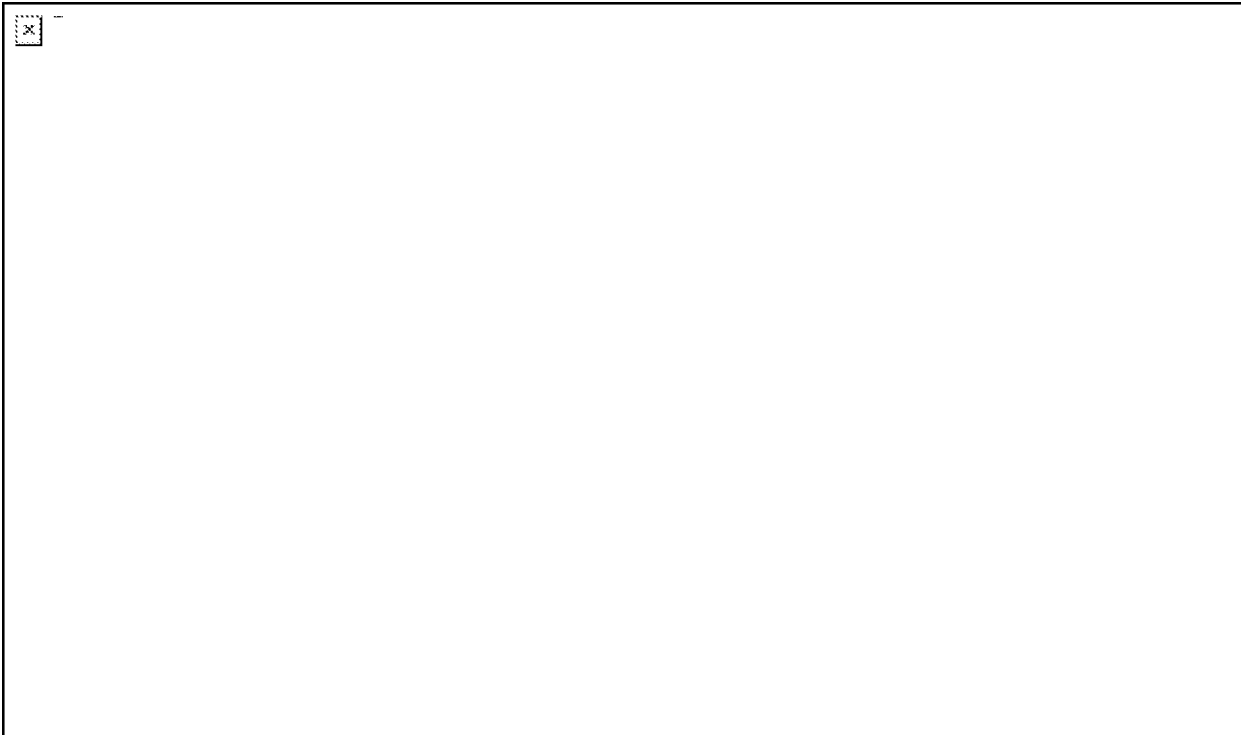
[0241]

[Table 12]

	
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[0242]

[Table 13]



[0243] By comparing with the examples 18-24 of a comparison of Table 4 which mentioned above the result of above-mentioned Table 12 - 13, a high discharge capacity is obtained, the capacity maintenance factor under hot environments is high in a room temperature list, and the sag by the self-discharge at the time of elevated-temperature storage is controlled, and the rechargeable battery of the examples 105-124 equipped with the gel nonaqueous electrolyte containing a non-aqueous solvent A or a non-aqueous solvent C is understood that bulging at the time of elevated-temperature storage is small.

[0244] On the other hand, as for the rechargeable battery of the examples 18-24 of a comparison, it turns out that the capacity maintenance factor in an elevated temperature all becomes low at a room temperature list compared with examples 105-124.

[0245]

[Effect of the Invention] As explained in full detail above, it can stop that according to the nonaqueous electrolyte and the nonaqueous electrolyte rechargeable battery concerning this invention control the generation of gas at the time of elevated-temperature storage and an initial-charge-and-discharge process, and a sheathing material blisters, and the self-discharge under hot environments can be controlled, and the remarkable effectiveness of being able to improve the cycle life in an elevated temperature in an ordinary temperature list is done so.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The sectional view showing the thin rechargeable lithium-ion battery which is an example of the nonaqueous electrolyte rechargeable battery concerning this invention.

[Drawing 2] The expanded sectional view showing the A section of drawing 1 .

[Drawing 3] The property Fig. showing <sup>1</sup>HNMR spectrum of the nonaqueous electrolyte of the thin nonaqueous electrolyte rechargeable battery of an example 35.

[Description of Notations]

- 1 -- Sheathing material,
  - 2 -- Electrode group,
  - 3 -- Separator,
  - 4 -- Positive-electrode layer,
  - 5 -- Positive-electrode charge collector,
  - 6 -- Positive electrode,
  - 7 -- Negative-electrode layer,
  - 8 -- Negative-electrode charge collector,
  - 9 -- Negative electrode,
  - 10 -- Positive-electrode terminal,
  - 11 -- Negative-electrode terminal.
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